ISSN 0-825-4591

PROCEEDINGS

TECHNOLOGY TRANSFER CONFERENCE

December 8 & 9, 1986

The Sheraton Centre

External Research Projects

PART A
AIR QUALITY RESEARCH

Organized by
Research Advisory Committee

Sponsored by

Corporate Resources Division
Ministry of the Environment
Ontario
CANADA

Goal Statement

"To achieve and maintain a quality of the environment - including air, water and land - that will protect human health and the ecosystem and will contribute to the well-being of the people of Ontario."

ACKNOWLEDGEMENTS

The Conference Committee would like to thank the speakers and organizers for their valuable contributions.

DISCLAIMER

The views and ideas expressed in these papers are those of the authors and do not necessarily reflect the views and policies of the Ministry of the Environment, nor does mention of trade names or commercial products constitute endorsement or recommendation for use.

INTRODUCTION

The Ontario Ministry of the Environment holds its annual Technology Transfer Conference to report and publicize the progress made on Ministry-funded projects. These studies are carried out in Ontario universities and by private research organizations.

The papers presented at the Technology Transfer Conference held in December 1986 are presented in Conference Proceedings. These Proceedings are divided into five parts corresponding to the conference sessions dealing with:
Part A: Air Quality Research ;
Part B: Water Quality Research;
Part C: Liquid & Solid Waste;
Part D: Analytical Methods; and
Part E: Environmental Economics.

This part is a collation of those papers presented at Session A of the Conference.

For further information on any of the projects, the reader is kindly referred to the Principal Investigators or to the Research Management Office at (416) 965-5788.

Paper No. **Page No.**

INTRODUCTION

PART A: AIR QUALITY RESEARCH:

FEATURE PAPERS

A **AN OVERVIEW OF ALBERTA ENVIRONMENT'S DEPOSITION RESEARCH PROGRAM** 1
H.P. Sims: Director, Alberta Environment's Research Management Division, Alberta, Canada.

B **MULTIMEDIA ANALYSIS AND ASSESSMENT OF ENVIRONMENTAL TOXIC AND CARCINOGENIC SUBSTANCES** ... 29
R. Harkov: Office of Science and Research, New Jersey Dept. of Environmental Protection, New Jersey, U.S.A.

SESSION PAPERS

1 **THE RAPID SCREENING OF MUNICIPAL REFUSE INCINERATOR FLYASH AND STACK GAS FOR PCDD/PCDF USING A TRANSPORTABLE TANDEM MASS SPECTROMETER (GC/MS/MS) SYSTEM** 45
B. Shushan[1], A. Ngo[1], V. Ozvacic[2], G. Wong[2], G. DeBrou[2], B. Bobbie[2], R. Clement[2], S. Thorndyke[3] and B. Chittum[4]. 1-SCIEX, 2-Environment Ontario, 3-ORF, 4-Willington Consultants.

2 **RETROSPECTIVE CORRELATION SPECTROSCOPY AND ITS APPLICATION TO ATMOSPHERIC MONITORING** 59
R.W. Nicholls, M. Amani, M. Mandelman and W. Morrow, York University, Toronto, Ontario.

3 **MEASUREMENT OF ATMOSPHERIC CONSTITUENTS BY TUNABLE DIODE LASER ABSORPTION SPECTROMETRY** 64
H.I. Schiff, York University, Toronto, Ontario.

4 **UPTAKE, DISTRIBUTION AND CLEARANCE OF SOLUBLE AEROSOLS IN THE HUMAN RESPIRATORY SYSTEM** 81
W.J. Megaw[1] and J.F. Hicks[2]. 1-York University, Toronto, and 2-Environment Ontario.

5 **EXPERIMENTALLY DETERMINED MUTATION RATES IN LUNG AS AN AIR QUALITY STANDARD** 92
J. Heddle, A. Bouch, C. Couch, H. Kaul, J. Gingerich and K. Jain, York University, Toronto, Ontario.

Paper No.		Page No.
6	**THE HAMILTON STUDY: EFFECTS OF FINE PARTICLES ON THE RESPIRATORY HEALTH OF SCHOOL CHILDREN** .... L.D. Pengelly, A. Kerigan, C. Goldsmith, W. Furlong and S. Toplack, McMaster University, Hamilton, Ontario.	106
7	**BIOLOGICAL MONITORING OF ENVIRONMENTAL GENOTOXICITY** .... M. Petras, J. Norsworthy, M. Vrzoc, and K. Hill, University of Windsor, Windsor, Ontario.	134
8	**FIELD AND LABORATORY VALIDATION OF A HIGH-VOL DENUDER FOR MINIMIZING PAH OXIDANT REACTIONS** .... C.S. Davies[1], S. Guerin[1], J. Marr[2] and M. Quilliam[2]. 1-Concord Scientific Corp., 2-McMaster University, Ontario.	177
9	**A PARTICLE-SIZE SPECIFIC ELEMENTAL MASS BALANCE FOR APPORTIONMENT OF AMBIENT AEROSOL SAMPLED WITH MULTISTAGE FRACTIONATORS** .... R.E. Jervis and T. Pringle, University of Toronto, Toronto, Ontario.	196
45	**MUTAGENICITY OF COMPLEX MIXTURES OF PAHS' IN AMBIENT AIR PARTICULATE MATTER** .... A.S. Raj and M. Katz, York University, Toronto, Ontario.	206
46	**DOSE - RESPONSE STUDIES OF GASEOUS POLLUTANTS OF FOOD CROPS** .... D.P. Ormrod and J. Petite, University of Guelph, Guelph, Ontario.	219
47	**PRODUCTION OF OZONE INSENSITIVE WHITE BEAN VARIETIES** .... T.E. Michaels, University of Guelph, Guelph, Ontario.	242
48	**NICKEL CARBONYL AMBIENT MONITOR** .... D.R. Hastie and H.I. Schiff, York University, Toronto, Ontario.	249
49	**ELEMENTAL COMPOSITION OF AIR PARTICULATES INSIDE AND OUTSIDE A BUILDING** .... P. Harvey, J.D. McArthur and G. Palmer, Queen's University, Toronto, Ontario.	263

Paper No. **Page No.**

50 **STUDY OF THE THERMAL REACTIONS OF PCDD ON FLYASH PARTICLES UNDER INCINERATOR CONDITIONS** 277
L.C. Dickson and F.W. Karasek, University of Waterloo, Waterloo, Ontario.

51 **CONTINUOUS EMISSION MONITORING FOR TOTAL HYDROCARBON AT SEWAGE SLUDGE INCINERATORS** 305
J. Kosch, AMKO Systems Inc., Thornhill, Ontario.

52 **STUDY OF THE SPATIAL DISTRIBUTION OF THE IMPACT OF SUDBURY SMELTING EMISSIONS** 314
E.A. McBean, J. Byrne, J. Donald and G. Farquhar, University of Waterloo, Waterloo, Ontario.

53 **CHARACTERIZATION OF BUILDING WAKE EFFECTS AT DARLINGTON NUCLEAR GENERATING STATION USING SULPHUR HEXAFLUORIDE AS A TRACER** 330
G. Ogram[1], H. Sahota[2] and P.K. Misra[2].
1-Ontario Hydro, 2-Environment Ontario.

PART B: WATER QUALITY RESEARCH

FEATURE PAPERS

A **PREDICTIVE MODELS IN HAZARD ASSESSMENT OF GREAT LAKES CONTAMINANTS OF FISH** 1
Dora R. May Passino: U.S. Fish and Wildlife Service, National Fisheries Centre - Great Lakes, Ann Arbor, Michigan, U.S.A.

B **CONTROL OF TOXIC TRACE CONTAMINANTS IN MUNICIPAL WASTE WATER TREATMENT PLANTS** 27
Henryk Melcer: Biological Processes Section, Wastewater Technology Centre, Canada Centre for Inland Waters, Environment Canada, Burlington, Ontario, Canada.

SESSION PAPERS

10 **TRACE ORGANIC CONTAMINANT REMOVAL FROM DRINKING WATER** 52
J. Hilton, MacLaren Plansearch Inc., Toronto, Ontario.

11 **THE ROLE OF ORGANIC CARBON IN CONTROLLING THE OCCURRENCE OF DENITRIFICATION IN GROUNDWATER** 67
R.C. Starr and R.W. Gillham, University of Waterloo, Waterloo, Ontario.

Paper No.		Page No.
12	**REPRODUCTIVE OUTCOMES IN SOUTHWESTERN ONTARIO, 1980 TO 1985** .... J. McD. Robertson, H. Chan and I. Fyfe, University of Western Ontario, London, Ontario.	82
13	**ORGANIC CONTAMINANT STRUCTURE - PROPERTY - TOXICITY RELATIONSHIPS FOR AQUATIC ORGANISMS** ...... S. Abernethy and D. Mackay, University of Toronto, Toronto, Ontario.	113
14	**EFFECT OF LEAD, CADMIUM AND MERCURY ON THE TISSUE OF YOUNG FISH AND RATS: DEVELOPMENT OF BIOINDICATOR** .... D.M. Nicholls, R. Angelow, K. Tiechert-Kuliszewska and G. Girgis, York Univesity, Toronto, Ontario.	138
15	**IN-SITU ASSESSMENT OF MIXED COPPER AND ZINC IMPACTS ON WHITE SUCKER (Castastomus Commersoni) POPULATIONS IN SEVERAL NORTHERN ONTARIO LAKES: AN EVALUATION OF THE ENVIRONMENTAL HEALTH APPROACH TO VALIDATING WATER QUALITY CRITERIA** ..... K.R. Munkittrick and D.G. Dixon, University of Waterloo, Waterloo, Ontario.	165
16	**THE FATE OF TOXIC ORGANIC CHEMICALS IN SEWAGE TREATMENT PLANTS** .... B. Clark, S. Salenicks, J. Glynn Henry and D. MacKay, University of Toronto, Toronto, Ontario.	176
17	**TOXICITY OF PENTACHLOROPHENOL TO ZOOPLANKTON** ...... N.K. Kaushik and G. Stephenson, University of Guelph, Guelph, Ontario.	192
18	**DEVELOPMENT OF A STANDARD CLAM BIOMONITORING METHODOLOGY FOR THE DETECTION OF TRACE CONTAMINANTS WITHIN WATERS OF THE ONTARIO GREAT LAKES REGION** .... A. Melkic, E. Greece and D. Lewis, Integrated Explorations Ltd., Guelph, Ontario.	205
54	**EVALUATION OF DATA ON THE EFFECTS OF HYDRAULIC CHARACTERISTICS AND EFFLUENT CHLORINATION ON THE INCIDENCE OF MICRO-ORGANISMS OF PUBLIC HEALTH SIGNIFICANCE IN RECEIVING WATERS** .... M. Palmer, Gore & Storrie Ltd., Toronto, Ontario.	219
55	**LISTOWEL ARTIFICIAL MARSH TREATMENT PROJECT** .... J. Herskowitz, S. Black and W. Lewandowski, Ministry of the Environment, Toronto, Ontario.	244
56	**A LOW PRESSURE HYDROCYCLONE FOR USE IN SEWAGE TREATMENT** .... J.D. Boadway, Queen's University, Kingston, Ontario.	267

Paper No. **Page No.**

57 THE EFFECTS OF RURAL AND SUBURBAN DEVELOPMENT ON SURFACE WATER QUALITY IN FIVE SELECTED SUBWATERSHEDS ON THE UPPER HUMBER RIVER 294
B. Hindley, R. Hubbard and S. Maude, Metro Toronto Conservation Authority, Toronto, Ontario.

58 HUMBER RIVER/BLACK CREEK: DETAILED BACTERIOLOGICAL WATER QUALITY STUDY EXAMINING THEIR IMPACT OF SEDIMENT AND SURVIVAL TIMES 347
P.L. Seyfried and E. Harris, University of Toronto, Toronto, Ontario.

59 FEASIBILITY OF PLANT HARVESTING IN WATER QUALITY AMELIORATION AND PHOSPHORUS MANAGEMENT IN SHALLOW IMPOUNDMENT 392
P. McKee, K. Clarke-Whistler and G. Gaspardy, Beak Consultants Ltd., Toronto, Ontario.

60 TWO BIOASSAYS FOR THE RAPID DETERMINATION OF THE EFFECTS OF DREDGED SEDIMENT DISPOSAL IN PRIMARY PRODUCTION AND PHOSPHORUS KINETICS IN OPEN WATERS 415
C. Ewing and C. Nalewajko, University of Toronto, Scarborough, Ontario.

61 STOCHASTIC ESTIMATION OF AMBIENT WATER QUALITY IN THE THAMES RIVER 438
V.A. Graham, T.E. Unny and L. Logan, University of Waterloo, Waterloo, Ontario.

62 OTTAWA RIVER NUCLEAR SPILL CONTINGENCY MODEL DEVELOPMENT: PHASE II 467
T. Gowda, M. Palmer, C. Arnoldi and R. Jarvis, Gore & Storrie Ltd., Toronto, Ontario.

PART C: LIQUID & SOLID WASTE RESEARCH

FEATURE PAPERS

A HAZARDOUS WASTE DESTRUCTION: AN OVERVIEW OF APPROACHES AND SHORTCOMINGS 1
E. Timothy Oppelt: Thermal-Destruction Branch, Alternative Technologies Division, U.S.-EPA, Cincinnati, Ohio, U.S.A.

B AN OUTLINE OF U.S.-EPA RESEARCH ON LAND DISPOSAL OF HAZARDOUS WASTE 26
Norbert Schomaker: Hazardous Waste Engineering Research Lab., US-EPA, Cincinnati, Ohio, U.S.A.

Paper No. **Page No.**

SESSION PAPERS

19 **ASSESSMENT OF A PROTOTYPE SYSTEM FOR PYROLYSIS OF REFUSE DERIVED FUEL** 38
S.J. Thorndyke, Ontario Research Foundation, Mississauga, Ontario.

20 **MUNICIPAL SOLID WASTE FEASIBILITY OF GASIFICATION WITH PLASMA ARC** 63
G.W. Carter, Resorption Canada Ltd., Ottawa, Ontario.

21 **SEWAGE SLUDGE COMPOST AS TURF FERTILIZER** 78
J.L. Eggens, Ontario Agricultural College, University of Guelph, Guelph, Ontario.

22 **WASTE MANAGEMENT PLANNING FOR PHARMACEUTICAL INDUSTRY - PHASE I: INVENTORY AND DATA COLLECTION** 85
R. Makhija and R. Stairs, Tent University, Peterborough, Ontario.

23 **DEVELOPMENT OF GUIDELINES FOR THE UTILIZATION OF INDUSTRIAL WASTE IN BACKFILL AND CONSTRUCTION APPLICATIONS** 94
G. Zukovs, Canviro Consultants Ltd., Toronto, Ontario.

24 **NUMERICAL AND LABORATORY MODELLING OF TWO-PHASE FLOW IN POROUS MEDIA: 1 - TWO-PHASE GASEOUS FLOW, 2 - TWO-PHASE LIQUID FLOW** 117
G. Farquhar, E. McBean, J. Byrne, W. Abbott and R. Kell, University of Waterloo, Waterloo, Ontario.

25 **DEVELOPMENT OF POLYSULFIDE TECHNOLOGY FOR TREATMENT OF CONCENTRATED SPENT CYANIDE LIQUORS** ... 144
J.J. Gaczarczyk, University of Toronto, Toronto,

26 **TREATMENT OF LANDFILL LEACHATE BY SPRAY IRRIGATION** 175
R. McBridge, A.M. Gordon, P. Groenvelt, T. Bates and K. King, University of Guelph, Guelph, Ontario.

27 **CO-DISPOSAL OF INDUSTRIAL AND MUNICIPAL WASTES: PART II** 192
D. Kirk and M. Lau, University of Toronto, Toronto, Ontario.

63 **HAZARDOUS ORGANIC CHEMICALS IN GROUNDWATER AT ONTARIO LANDFILLS.** 206
J.F. Baker and J. Cherry, University of Waterloo, Waterloo, Ontario.

Paper No. **Page No.**

64 **DISPERSION OF THE STOUFFVILLE CONTAMINANT PLUME** 229
I. Proulx, R.N. Farvolden and E. Frind, University of Waterloo, Waterloo, Ontario.

65 **DEVELOPMENT OF DESIGN CRITERIA FOR OPTIMAL RECOVERY OF LEACHATE UNDER SANITARY LANDFILLS** 243
L. Arnaud, E. Frind, R. Farvolden and R. Gillham, University of Waterloo, Waterloo, Ontario.

66 **AN INVESTIGATION INTO THE REDOX CONDITIONS OF A LANDFILL LEACHATE PLUME CONTAINING VOLATILE ORGANICS, GLOUCESTER, ONTARIO** 272
L. Elliott, J. Develin, F. Michaels and W. Gorman, Queen's University, Kingston, Ontario.

67 **EFFECTS OF INCREASING AMOUNTS OF NON-POLAR ORGANIC LIQUIDS IN DOMESTIC WASTE LEACHATE ON THE HYDRAULIC CONDUCTIVITY OF CLAY LINERS IN SOUTHWESTERN ONTARIO** 294
R.M. Quigley and F. Fernandez, University of Western Ontario, London, Ontario.

68 **ASSESSMENT OF CONTAMINANT MIGRATION FROM INDUSTRIAL SOURCES DISCHARGING TO THE WELLAND RIVER** 315
M. Dickman, P. Hayes and I. Brindle, Brock University, St. Catherines, Ontario.

69 **EVALUATION OF CONTAMINANT VELOCITY GROUNDWATER IN LOW PERMEABILITY FRACTURE SHALE** 338
E. Sudicky, R. Blackport and J. Cherry, University of Waterloo, Waterloo, Ontario.

70 **GEOMECHANICAL INVESTIGATION OF NEAR-SURFACE FRACTURES IN CLAY TILLS** 349
M. Dusseault and A.Vorauer, University of Waterloo, Waterloo, Ontario.

71 **ORIGINS OF ELEVATED CHLORIDE CONCENTRATIONS IN GROUNDWATER SYSTEMS** 376
P.E. Pilon and K.W.F. Howard, University of Toronto, Scarborough, Ontario.

PART D: ANALYTICAL METHODS

FEATURE PAPERS

A **TRENDS IN MULTI-ELEMENT ANALYSIS: THE ROLE OF ICP-MS IN ENVIRONMENTAL APPLICATIONS** 1
Barry French, Institute for Aerospace Studies, University of Toronto, Toronto, Ontario, Canada.

Paper No. **Page No.**

B **DETECTION OF HYDROXYLATED NITRO-POLYNUCLEAR AROMATIC HYDROCARBONS AND KETONES IN AN AMBIENT AIR PARTICULATE EXTRACT USING BIOASSAY-DIRECTED FRACTIONATION** 31
Marcia G. Nishioka and Corrine C. Howard, Analytical Chemistry Section, Battelle Columbus Division, Columbus, Ohio, and Joellen Lewtas, U.S. - EPA, North Carolina, U.S.A.

SESSION PAPERS

28 **DIRECT SOLID SAMPLE ANALYSIS WITH THE DIRECT SAMPLE INSERTION DEVICE, PROMISE AND PROBLEMS** 64
E. Salin and R.L. Sing, McGill University, Montreal, Quebec.

29 **SCREENING METHODS FOR AIR AND WATER SAMPLES: APPLICATION OF INDUCTIVELY COUPLED PLASMA MASS SPECTROMETRY (ICP/MS) TO ELEMENTAL ANALYSIS** 74
J. Van Loon and B.French, University of Toronto, Toronto, Ontario.

30 **DEVELOPMENT OF SELENIUM ANALYSIS METHODOLOGY AT NG/L LEVELS FOR SOFT WATERS SUBJECT TO ACIDIC PRECIPITATION** 97
L.M. Brown and J. Wehr, University of Western Ontario, London, Ontario.

31 **EVALUATION AND OPTIMIZATION OF A TOC ANALYZER USING UV - PERSULPHATE DIGESTION** 111
R.D. Evans, Trent University, Peterborough, Ontario.

32 **DEVELOPMENT OF AN ULTRASONIC NEBULIZER FOR STABLE AND REPRODUCTIVE PRODUCTION OF AEROSOLS FOR ATOMIC SPECTROMETRIC ANALYSIS** 112
J.C. Van Loon, University of Toronto, Toronto, Ontario.

33 **DEVELOPMENT OF RECOMBINANT DNA PROBES TO DETERMINE THE ORIGIN OF FECAL STREPTOCOCCI AT THE TORONTO AREA BEACHES** 133
W.C. Bradbury, M.A. Marko, L. Papageorgiou, D. Leight and D. Rego, University of Toronto, Toronto, Ontario.

34 **PLANT BIOASSAYS FOR THE DETECTION OF ENVIRONMENTAL MUTAGENS** 147
Wm. F. Grant, McGill University, Montréal, Quebéc.

35 **A BIOLOGICAL INDICATOR SYSTEM TO IDENTIFY GENOTOXICITY OF IN-PLACE POLLUTANTS** 167
D.R. Hart, J. Fichko, M. Brinkman and P. McKee, IEC Beak Consultants Ltd., Mississauga, Ontario.

Paper No.		Page No.
36	**FRESHWATER CLAMS AS MONITORS OF VARIATION IN ENVIRONMENTAL ACIDITY AND TRACE METAL LEVELS** ...... R.H. Green, S. Hinch and R. Bailey, University of Western Ontario, London, Ontar[illegible].	189
72	**ANALYSIS OF DIOXINS AND FURANS IN FISH AND OTHER BIOTA** .... F.W. Karasek, T. Thompson, D. Schelenberg and K. Naikwadi, University of Waterloo, Ontario.	215
73	**DEVELOPMENT OF COST-EFFECTIVE PROTOCOL FOR ROUTINE ANALYSIS FOR TRACE ORGANIC CONTAMINANTS IN MUNICIPAL WPCP RAW SEWAGE AND FINAL EFFLUENT** .... C. Chan[1], J. Martin[1], P. Pond[1], G. Rees[2], and T. Ho[2]. 1-Mann Testing Labs. Ltd., 2-Environment Ontario.	234
74	**APPLICATION OF GC HELIUM MICROWAVE PLASMA DETECTION TO THE RAPID SCREENING OF CHEMICAL WASTE** .... M. Danszinger, Barringer Magenta Ltd., Rexdale, Ontario.	255
75	**DEVELOPMENT OF METHODS SUITABLE FOR THE USE IN THE AMES SALMONELLA MUTAGENICITY ASSAY FOR THE COLLECTION OF ORGANICS PRESENT IN GROUNDWATER AND LANDFILL SITE MATRIX MAERIALS** .... G.H. Thomas, A. Horton and K. Matsummura, Ontario Research Foundation, Mississauga, Ontario.	271
76	**SYNTHESIS OF OXYGEN AND SULPHUR PAHS OF INTEREST IN ENVIRONMENTAL POLLUTION** .... E. Lee-Ruff and F. Ablenas, York University, Toronto, Ontario.	294
77	**DEVELOPMENT OF A ROBOTIC WORKSTATION FOR THE ROUTINE ANALYSIS OF ORGANICS IN BIOLOGICAL TISSUES USING ACID DIGESTION AND SOLVENT EXTRACTION METHOD** .... C. Chan[1], J. Martin[1], G.Ladwig[1], G. Rees[2], and G. Crawford[2]. 1-Mann Testing Labs Ltd., 2-Environment Ontario.	298
78	**SEPARATION AND IDENTIFICATION OF ORGANIC COMPOUNDS IN EXTRACTS OF AIR PARTICULATES BY HPLC AND GC/MS** .... K.P. Naikwadi, G. Charbonneau and F.W. Karasek, University of Waterloo, Waterloo, Ontario.	331

Paper No. **Page No.**

79 QUANTITATIVE DETERMINATION OF SELECTED PAHS' BY SHPOL'SKII AND JET-COOLED SPECTROSCOPY 355
C.M. Sadowski, J. Lai, H. Malle, S. Filseth and F. Morgan, York University, Toronto, Ontario.

80 NEW SYNTHETIC METHODOLOGY FOR THE EXPEDIENT PROVISION OF PURE PAH ANALYTICAL STANDARDS 384
V.A. Snieckus, University of Waterloo, Waterloo, Ontario.

PART E: ENVIRONMENTAL ECONOMICS

FEATURE PAPER

A THE ENVIRONMENT OF ECONOMICS - PAST PRESENT AND FUTURE ROLES OF ECONOMICS IN ENVIRONMENTAL MANAGEMENT 1
Clifford Russell, Director, Institute for Public Policy Studies, Vanderbilt University, Nashville, Tennesee, U.S.A.

SESSION PAPERS

37 ABATEMENT COST FUNCTIONS - THE WORKHORSE OF ENVIRONMENTAL MANAGEMENT 18
J. Donnan, C. Griffith, S. Glover and M. Dandele, Policy & Planning Branch, Ministry of the Environment, Toronto, Ontario.

38 MEASURING THE SOCIAL COSTS OF ELECTRICAL EXPORTS AND COST RECOVERY OPPORTUNITIES OF ENVIRONMENTAL PROTECTION OF ONTARIO HYDRO 39
W. Wianko and B. Green, Ontario Hydro, Toronto, Ontario.

39 QUÉBEC'S EXPERIENCE WITH THE ECONOMIC EVALUATION OF ENVIRONMENTAL REGULATIONS - WHAT LESSONS HAVE BEEN LEARNED 65
C. Sauvé, Ministére de l'Environment, Sainte-Foy, Québec.

40 3M'S POLLUTION PREVENTION PAYS PROGRAM 77
A.G. Mills, 3M Canada Inc., London, Ontario.

41 THE BENEFITS OF REDUCING LEAD IN U.S. DRINKING WATER 87
R. Levin, U.S.-EPA, Washington, D.C., U.S.A.

Paper No.		Page No.
42	**ECONOMIC EFFECTS OF REDUCED FOREST GROWTH IN THE UNITED STATES' FOREST ECONOMY AND ON CANADIAN-U.S. LUMBER TRADE** .... J.M. Callaway, Jr., Battelle Northwest Labs, Richland, Washington, U.S.A.	112
43	**SOME ECONOMICS OF THE GRAND CANAL** .... A. Muller, Department of Economics, McMaster University, Hamilton, Ontario.	129

AN OVERVIEW OF ALBERTA ENVIRONMENT'S ATMOSPHERIC DEPOSITION PROGRAM

H.P. Sims, G.A. Singleton, H.S. Sandhu, and B.L. Magill

1. INTRODUCTION

Atmospheric emissions of pollutants, their deposition, and potential long-term detrimental effects on the environment have not only become a serious scientific issue, but a focus of significant public concern in Alberta. Nevertheless, industrial development is dictated by economic opportunity and cannot wait for long-term research projects to provide all of the answers to possible problems. In many cases, we must rely on judgement and external experiences to allow promotion of development goals without sacrificing critical components of our environment. We are aware that our perspectives of the relationship between environmental quality and industrial development are diverse and vary from region to region. However, the concern for environmental quality has never been higher in our history than at present, and determined efforts by the public to have an influential role in the decisions that affect the fate of our environment are rightfully increasing.

With the use of emission abatement strategies, local ground level concentrations have decreased in the vicinity of new stationary sources. However, the potential for long-term, progressive, subtle impact on the environment remains. A number of issues and concerns have been identified in documents published by Alberta Environment (Appendix I). Relative to Alberta, our knowledge regarding medium and long-range transport of air pollutants/acid rain and the environmental and human health effects of long-term, low-level emissions is presently limited. Research and monitoring/surveillance programs need to be expanded and implemented to overcome our knowledge deficiencies. To facilitate this, Alberta Environment established three research programs (Departmental Acid Deposition; Air Quality; and Environmental Contaminants).

2. DEPARTMENTAL ACID DEPOSITION PROGRAM

Acid-forming emissions, such as oxides of sulphur and nitrogen, can be transported from a few to thousands of kilometers. Because of the dramatic deleterious environmental effects observed at Sudbury, Ontario; Trail, British Columbia; and in the vicinity of many point sources in the United States, it was generally believed that emissions resulted mainly in local environmental impacts. However, scientific evidence has been obtained to show that transport of these emissions occurs over long distances, such as from the Ohio River Valley through the northeastern United States into eastern Canada, from the United Kingdom into Norway, and from the Ruhr Valley in West Germany into Sweden. Similarly, emissions originating in Alberta are transported to areas downwind of major sources, where ecosystems may be sensitive to acid deposition (Sulphur Gas Emissions in the Boreal Forest: The West Whitecourt Case Study, 1978; Environmental Sulphur Research in Alberta: A Review, 1980). The present and potential impacts of these emissions are not well understood. Some of the concerns are: (a) acidification of surface waters and the potential consequences for aquatic biota, including fish; (b) acidification of soils and their influence on the total watershed, vegetation and aquatic systems; (c) direct effects on agricultural crops and forest tree species; and (d) direct and indirect effects on human and animal health.

2.1 OBJECTIVES OF THE PROGRAM

The overall objective of the acid deposition program is to design, co-ordinate, and implement a research and monitoring program concerning acid-forming emissions and their ecological effects in Alberta. The program will provide scientific information for evaluating and reviewing Alberta's current air quality standards, emission guidelines, and regulatory controls with respect to socio-economic and environmental consequences of atmospheric pollutants to satisfy the concerns of Albertans.

Specific objectives of the Departmental program are to:

1. Undertake routine monitoring of air, water, soils, and vegetation to determine short- and long-term trends in environmental quality;

2. Characterize sensitive environmental components and develop methodologies to (a) identify and/or predict environmental deterioration caused by acid-forming substances in Alberta; and (b) determine when environmental deterioration begins and whether or not the effects are reversible;
3. Characterize, separate, and quantify the contributions of emissions, from local sources and from the medium- and long-range pollutant transport, to environmental effects of acidification;
4. Review, co-ordinate and implement a research program concerning acid-forming emissions and their short- and long-term environmental and health effects;
5. Determine the socio-economic impacts of acidification and develop a scientific basis and approach for preventive and/or mitigative strategies and environmental protection taking into account the socio-economic factors;
6. Provide support to and integration of the research, monitoring, and other activities of the Departmental Committee on Acid Deposition, Alberta Government/Industry Acid Deposition Research Program (ADRP), the Western and Northern Canada LRTAP Technical Committee (W&NC-LRTAP), and other agencies.

2.2 PROGRAM COMPONENTS

The Acid Deposition Research Program is comprised of five distinct but integrated components:

1. Alberta Environment's Acid Deposition Effects Research Program;
2. The Alberta Government/Industry Acid Deposition Research Program;
3. Western and Northern Canada LRTAP;
4. Departmental Monitoring Program; and
5. Inhalation Toxicology and Animal Health Program.

Each of these components is discussed in the ensuing sections.

2.3 ALBERTA ENVIRONMENT'S ACID DEPOSITION EFFECTS RESEARCH PROGRAM

Forest decline evident in Europe and in eastern North America has been attributed to acid deposition, although scientists still debate which of several mechanisms may be responsible for the decline. In Alberta, government and the public are concerned whether or not a similar decline will occur in Alberta's forests as a result of acid deposition. Alberta Environment's acid deposition effects research program was developed to assess long-term environmental impacts of industrial developments in the oil sands region of northeastern Alberta on forest and aquatic ecosystems. Research has been co-ordinated under the auspices of the Alberta Oil Sands Environmental Research Program (AOSERP).

2.3.1 Program Development 1975 to 1985

The initial phase of the program (1975 to 1980) accumulated baseline information required to quantify and characterize existing environmental conditions, primarily dominant soil and vegetation types. This baseline information was to be used to identify ecosystems most likely to be impacted by acid deposition and to assess the impact of industrial development on these ecosystems.

Air quality and meteorological networks were established to collect data on local air mass trajectories and climate. These data were used in the development and verification of an air quality model capable of predicting the ground level concentrations of pollutants based on varying meteorological conditions and emission levels. The model was used to delineate areas of maximum SO_2 loading, and therefore subject to potential acidification and long-term environmental damage.

To further address the environmental impact of industrial development, precipitation chemistry monitoring networks were established. The accumulated snowpack and event rainfall were extensively sampled and analyzed to determine: (1) trends in the ionic and particulate concentration of precipitation resulting from industrial emissions, and (2) deposition patterns and spatial variability of wet deposition pollutant loadings.

Although baseline information was collected on the sensitivity of terrestrial and aquatic ecosystems to pollutant deposition, strategies had not been implemented to ensure the interdisciplinary, integrated approach needed to understand the complex interrelationships between atmospheric and biological processes. In a review of the research and monitoring activities undertaken during 1975 to 1980, research deficiencies were identified and future research recommended. Specific recommendations were:

1. To characterize and quantify regional and local source emissions to ascertain their relative contribution to environmental acidification;
2. To integrate episodic air quality data with receptor response in order to (a) characterize sensitive environmental ecosystems and (b) develop methodologies to identify and/or predict measurable short- and long-term effects of acidic or acidifying substances on terrestrial and aquatic ecosystems;
3. To develop a scientific basis and approach for preventive strategies and long-term environmental protection/management; and
4. To co-ordinate departmental research on acid deposition with other private and public agencies in Alberta and the rest of western Canada.

From 1980 to 1985, the program concentrated on addressing these research deficiencies, especially characterizing and quantifying the ecological effects of acidic and acidifying substances. Considerable effort and resources were expended to develop a more thorough understanding of the atmosphere-biosphere interface. Research consisted of field and laboratory investigations of plant responses to emitted pollutants. Specific projects were geared to the accurate and frequent measurements of pollutant concentration occurrences and their interface with physiological, phenological and productivity responses in vegetation species. A second major interface, between soil nutrients, microbiological processes and vegetation was also being studied.

With respect to atmospheric research, regional surveys to sample and chemically analyze wet deposition were continued. Wet deposition, however, is only one of two major mechanisms in the transfer of pollutants from source to the ecosystem receptor. Air pollutants released into the atmosphere are deposited continuously and cumulatively through both dry and wetfall processes. Methodologies and instrumentation technology for measuring dry deposition to a forest canopy were developed and implemented on an experimental basis. However, more evaluation and research are required before dry deposition monitoring techniques can be employed on a routine operational basis. In conjunction with these studies, research to determine the transport, dispersion, and transformation rates of sulphur and nitrogen oxides emissions were undertaken to facilitate the investigation of the medium- to long-range transport of acid-forming emissions from a major emission source in the oil sands area.

A summary report for research and monitoring work carried out in the oil sands area between 1975 to 1985 is in preparation.

In the 10-year period 1975 to 1985, research demonstrated clearly the high degree of natural variability in ecosystem parameters, especially in forest ecosystems, which would make it difficult to detect subtle changes in the ecosystem occurring as a result of low acid-forming emission levels. Therefore, it became clear that a new strategy was required for evaluation of acid deposition effects in the oil sands area.

2.3.2 The New Five-Year Research Plan

Effects research can only be done meaningfully in the oil sands area using long-term monitoring techniques in which biological variability is statistically accounted for. Before embarking on any additional new research efforts in the northern forested areas, Alberta Environment felt it was necessary to undertake a detailed review of the existing research studies and make use of the world literature reviews conducted in the Government/Industry Acid Deposition Research Program. The Department has completed the review and produced a new strategy to develop biomonitoring indices which will be used to monitor effects of low levels of acid-forming emissions over the medium- and long-term.

A new five-year plan for research in the oil sands area was initiated in 1986/87. The five-year research needs of this program are summarized in **Table 1.** This new program, which is described in the following sections, includes the following activities and will guide acid deposition research in northern forested areas of Alberta until at least 1991:

1. Evaluation of biomonitoring indices for terrestrial and aquatic systems;
2. Selection of biomonitoring methods and compilation of a data base over a deposition gradient of acid-forming emission; and
3. Investigation of data to develop empirical relationships between emissions and biomonitor response.

The effects research program is designed to address the question; is there measurable environmental damage due to acidification which can be monitored over the medium and long-term? If ecosystem damage is occurring, the hypothesis is that the pollutant loading and some corresponding quantitative measurement of damage will vary significantly along the deposition gradient. In order to identify an appropriate pollution gradient and determine deposition inputs for effects research, atmospheric research will determine sources, distribution, and deposition characteristics of the existing acid-forming emissions in the oil sands area. A monitoring program will be designed to determine the (1) horizontal and vertical distribution of atmospheric gaseous and particulate matter within and above the forest canopy, and to the soil and aquatic ecosystems; (2) wetfall deposition at canopy height and ground level to provide information on throughfall and available input to the soil and groundwater; and (3) microclimate of the receptor area.

Source apportionment studies and projects to upgrade emission inventories by collecting information on fugitive and low-level emissions are proposed in order to quantify and characterize the total emission burden resulting from Syncrude, Suncor, and other anthropogenic sources in the oil sands area. This will enable Alberta Environment to assess the environmental impacts of present and future oil sands development.

Table 1. Five-year research needs for Alberta Environment's Acid Deposition Research Program.

---

1. Organized evaluation and synthesis of existing information on atmospheric processes, deposition and receptor responses, as they relate to Alberta.

2. Description of regional (provincial) scale meteorology and atmospheric processes.

3. Characterization of the physics and chemistry of selected Alberta point source plumes, with simultaneous ground level measurements.

4. Characterization and quantification of atmospheric deposition of beneficial and deleterious chemical constituents into Alberta ecosystems.

5. Identification and qualitative and quantitative characterization of sensitive receptors and processes related to acid deposition (laboratory and field).

6. Development of numerical methodologies to correlate atmospheric processes and pollutant deposition to effects on total ecosystems (i.e., receptor response), using an integrated approach. This should evolve into predictive capabilities to forecast air pollutant-induced ecosystem impacts.

7. Characterization and quantification of the effects of atmospheric pollutants on human/animal health.

8. Interpretation of program results to determine socio-economic and environmental consequences and mitigation strategies which will assist decision makers in the development of public policy and regulatory guidelines and controls to ensure and maintain environmental quality and human/animal health.

Biomonitoring indices selected for impact assessment research will have to be evaluated first for their spatial and temporal variability. Vegetation research will involve testing the variability of biological indicators of acidification, such as needle length, needle retention, and seed viability. Provided that real impact-associated differences can be discriminated, the appropriate biomonitoring indices will be incorporated into a monitoring program and tested on a regional basis. A further restraint is that the monitoring indices must be feasible for use in medium-term (up to 25 years) programs.

Although some routine monitoring of soil parameters may be done for site characterization purposes, detailed monitoring of a wide range of soil parameters for detection of impacts in the medium-term is not considered advisable. Rather, soil effects research will concentrate on the identification of those soil components that buffer against long-term changes resulting from acid-forming emissions. A model would be developed to determine the buffering capacity of sensitive forest soils, and what effects current and potential long-term loadings of acid-forming substances have or could have on soil chemistry. Predictions would be made as to how long, at assumed loading levels, it would take to cause major changes in soil chemistry and especially nutrient cycling capabilities.

An investigation will be made of the modelling techniques available for translating pollutant loading measurements or predictions to changes in water chemistry. Modelling techniques will be adopted to provide the following information:

1. Area loading (atmospheric) translated into predictable changes in water chemistry;
2. Time frame for observable changes in water chemistry; and
3. Rate at which acidification and changes in water chemistry would proceed.

2.4 GOVERNMENT/INDUSTRY ACID DEPOSITION RESEARCH PROGRAM

The formation of the Government/Industry Acid Deposition Research Program (ADRP) in 1985 is the result of a 10-year evolution to study and address the environmental consequences of acid-forming emissions on our environment. Public concern regarding effects of emissions from sour gas wells in southwestern Alberta on agricultural productivity and human health has been an integral part of this evolution. ADRP is an $11 million undertaking by the Province, industry (Canadian Petroleum Association, Alberta Power, Edmonton Power, Transalta Utilities) and the Energy Resources Conservation Board. Research is focussed on the agricultural effects of two principal gas groups, oxides of sulphur and nitrogen, and on human health effects. The research on agricultural effects is jointly funded by Alberta Environment, industry (Canadian Petroleum Association, Alberta Power, Edmonton Power, Transalta Utilities), and the Energy Resources Conservation Board. The human health research was completely funded by Alberta Social Services and Community Health.

The first critical phase of the agricultural research component, which spans a period of 32 months, will involve:

1. An initial assessment of the potential impact of emissions on Alberta's environment including local and regional air quality assessments. Three sites have been selected to monitor air quality parameters; a background site (Fortress Mountain, 100 km west of Calgary) to monitor air quality entering the province, and two sites in the study area (Crossfield, 30 km north and northeast of Calgary) representative of downwind and regional air quality;
2. An inventory of sulphur oxide and nitrogen oxide emissions in Alberta; and
3. A world literature review in the biological sciences on the effects of acid deposition on vegetation, soils, and surface and groundwaters. This will provide a comparative basis for a 'first order' assessment of the current status and future potential for acidification in Alberta.

The last two tasks are nearing completion and reports should be available in 1987.

The human health component of the program was designed to address the specific and long-standing health concerns of residents in the southwestern towns of Twin Butte, Hill Spring, Mountain View, and Glenwood (Index Area) to determine if residents of the Index Area are healthier or less healthy than other Albertans. Some residents have had long-standing health complaints which they attribute to sour gas plant operations. Two other communities served as controls - one exposed to "pollution" (Didsbury, Carstairs, Crossfield, Irricana) and one not exposed (Stirling, Raymond). A comprehensive health assessment was undertaken using questionnaires and physical examinations. Over 3600 residents were medically examined in the summer of 1985 by the team of doctors headed by Dr. W.O. Spitzer of McGill University. While the study did not deal with cause/effect relationships, it established that the health of residents in the Index Area was not significantly different from other Alberta communities. The human health study, the Medical Diagnostic Review, was completed in June 1986 and the final report is currently being reviewed.

In addition to the Medical Diagnostic Review, an occupational epidemiology feasibility study, which will focus on the occupational work force of the sweet, sour, and thermal gas industry, will attempt to determine whether acute or chronic exposure to sour gas or its by products has significantly affected the health of the workers. To ensure the scientific integrity of the program, scientific advisory boards comprised of international environmental and medical scientists provide advice on and peer review of the program. In recognition of the value of public views of the program, a public advisory board has been formed to facilitate involvement from and communication with the general public and environmental interest groups.

2.5 WESTERN AND NORTHERN CANADA LRTAP PROGRAM

The departmental program provides the Alberta focus for the Western and Northern Canada Long Range Transport of Air Pollutants (W&NC-LRTAP) federal/interprovincial program which is investigating the medium- and long-range transport of air pollutants and their possible environmental effects.

The national and provincial governments of Canada have a tradition of joint action on environmental issues, resulting in cost-effective research and monitoring programs and a uniform approach to problems regardless of provincial boundaries. The acid rain program in western and northern Canada is a good example.

British Columbia, Alberta, Saskatchewan, Manitoba, Northwest Territories, and Canada first held joint consultations on the acid rain issue in 1980. By 1982, they, as a consequence of their commitment to undertake research and monitoring programs to protect sensitive ecosystems from potential acidification, signed an agreement for a three-year research program covering the period 1982 to 1985. The program's objectives included identifying current conditions in western Canada and providing information necessary to develop appropriate management strategies. The six program priorities and the major accomplishments attained during this period are delineated in the ensuing points:

1. Maps of aquatic sensitivity
   a. methodologies/criteria for determining sensitivity were developed; and
   b. preliminary maps completed.
2. Maps of soil and geology sensitivity
   a. methodologies/criteria for determining sensitivity were developed; and
   b. preliminary maps completed.
3. Monitoring of background precipitation
   a. standard protocols developed; and
   b. monitoring network expanded to 62 stations.
4. Modelling of atmospheric deposition patterns
   a. long-range models applied to western Canada and deposition maps produced; and
   b. mesoscale modelling workshop held to review and recommend mesoscale models for application in western Canada.
5. Emission inventories of sulphur dioxide and nitrogen oxides
   a. inventories regularly updated; and
   b. standardization of inventory data base pursued.

6. Monitoring of surface waters and soils in data sparse areas
    a. data base expanded; and
    b. standard water sampling methodologies pursued.

In 1984, W&NC-LRTAP agreed to continue co-operative action on a strategy for acid deposition to protect sensitive ecosystems from potential acidification. The identified research priorities for the subsequent three-year program 1985 to 1988 provide for: (1) the continuation and tailoring of the monitoring activities for parameters considered to be of special significance in western Canada, (2) the establishment of deposition standards suitable for the sensitivity of our environment, and (3) the investigation of deposition models and control models which will allow evaluation of the impact of individual sources, and the most cost-effective manner of implementing a control program. These priorities are:

1. Monitoring of air, rain, and snow;
2. Emission inventory update;
3. Deposition criteria/target loading for western Canada;
4. Medium-range transport/deposition models;
5. Background ion concentrations and the influence of dust on precipitation chemistry and total deposition loadings;
6. Dry deposition measurements;
7. Monitoring of sensitive surface waters and terrestrial environments; and
8. Evaluation of impact and assessment of control technology.

Projects undertaken by the Department to address the high priority needs identified by W&NC-LRTAP are highlighted in the Western and Northern Canada LRTAP annual reports.

2.6 DEPARTMENTAL MONITORING PROGRAM

The Department is involved in an extensive monitoring program of soil, water, air, and precipitation quality as part of its mandate to protect the environment. Monitoring of pollutants is conducted by line divisions within Alberta Environment to assist the Department in setting emission standards and determining compliance with existing regulations.

2.6.1 Precipitation Quality

The precipitation quality monitoring program was initiated in 1978 by the Air Quality Control Branch, Pollution Control Division, Alberta Environment. The objective of the program is to monitor the chemical characteristics of rain and snowfall which are representative of different regions in Alberta. The parameters of particular importance are the acidity or pH of precipitation and the sulphate and nitrate deposition rates which are directly related to the acid rain issue.

From 1978 to 1984, there were six provincial precipitation stations in the network. They were located at Beaverlodge, Calgary, Edmonton, Red Deer, Suffield, and Whitecourt. During 1985, three additional stations at High Level, Cold Lake, and Kananaskis were put into operation. It is intended that these three stations will provide additional information about the incoming background chemical contributions to precipitation events.

Besides the nine-station provincial network, the federal government operates five precipitation quality monitoring stations in Alberta under the CANSAP program (Canada Network for Sampling Precipitation). Their stations are located at Coronation, Edson, Fort McMurray, Lethbridge, and Rocky Mountain House. All stations in both networks collect monthly samples using automatic rain and snow collectors. Their data are directly comparable. Measurements of pH and major ionic concentrations are made on each accumulated monthly sample. The quality of the precipitation is assessed based on the different parameters: acidity from pH, acid-forming emission contributions from sulphate and nitrate concentrations, dust-related contributions from calcium and magnesium concentrations, and salt contributions from sodium concentrations.

In 1986, the CANSAP Program was replaced by the CAPMON Program which collects precipitation on a daily event basis rather than monthly. The only CAPMON station in Alberta, at this time, is located at Esther.

The monitored data from the federal network and the provincial network supplement each other to increase the coverage in Alberta. The locations of all stations in Alberta are illustrated in Figure 1. The accumulated data base allows the detection of any significant changes in

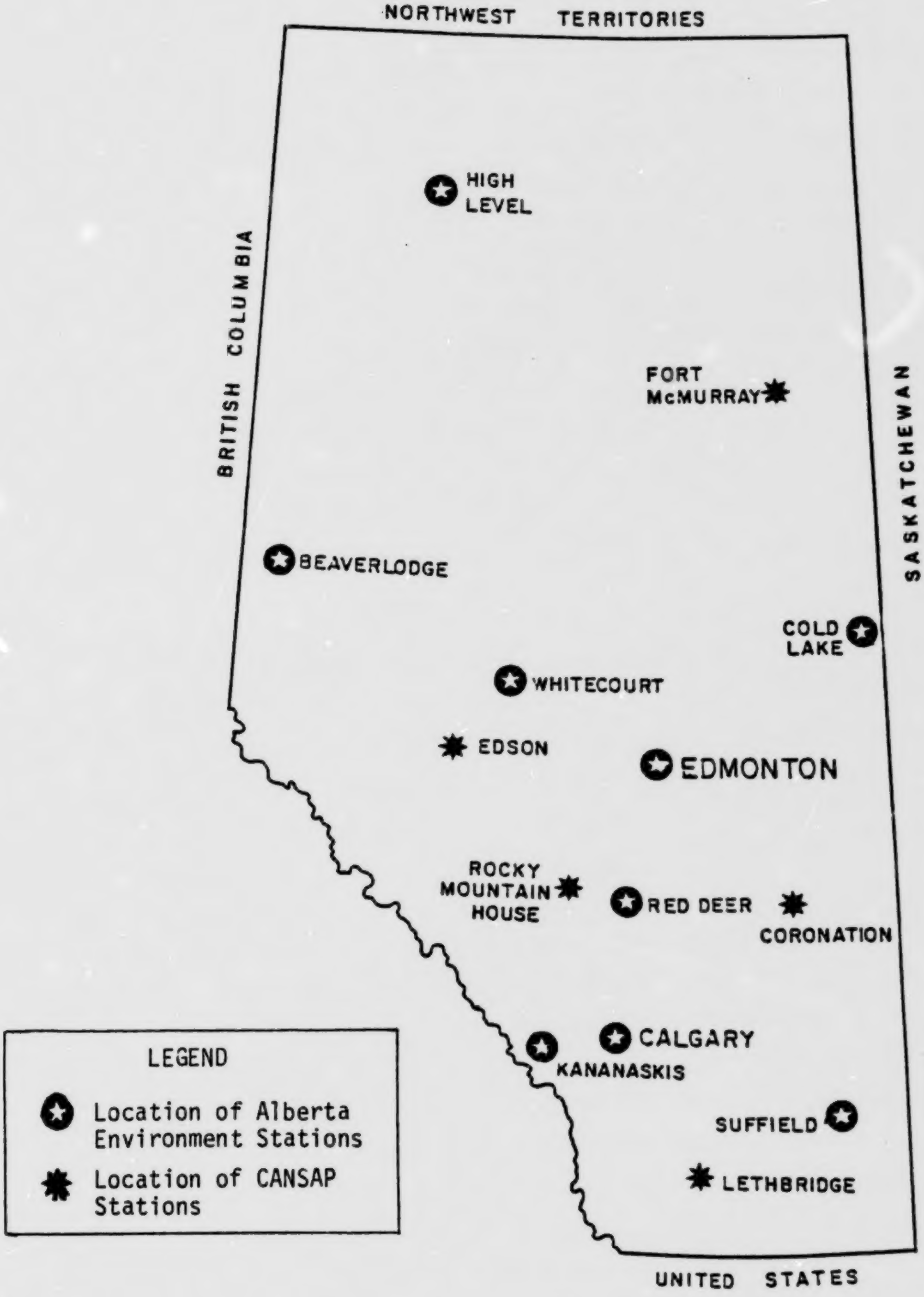


Figure 1. Location of precipitation quality monitoring stations in Alberta.

precipitation quality that may occur as a result of industrialization or long-range transport of the acid-forming pollutants.

Annual reports summarizing the data from the federal and provincial stations are published by the Air Quality Control Branch, Pollution Control Division, Alberta Environment.

2.6.2 Exposure Stations

The Exposure Station Program consists of 2112 total sulphation and 1276 hydrogen sulphide static exposure stations. These monitors are primarily located in and around urban centres and industrial areas of the province and are used to identify trends. Chemical analysis is done by the Alberta Environmental Centre (Vegreville), and the results are expressed as SO_3 equiv. mg/day/100 cm^2.

2.6.3 Soil Monitoring

Long-term soil acidification monitoring in Alberta carried out by Earth Sciences Division, Soil Protection Branch, began in September 1981. Monitoring plots have been established at eight different areas of the province (Rocky Mountain House, Fort McMurray, Twin Butte, Cold Lake, Esther, High Prairie, Devon, and Bruderheim) between 1981 and 1984 (Figure 2). The reason for establishing this program was to provide an early warning of the potentially adverse effects of atmospheric acid deposition on Alberta's soil resource. The objective of this program is to detect subtle changes in soil properties indicative of potentially significant long-term changes in the ability of soil to sustain plant growth. All sites will be resampled once every four years. The two principal components of the monitoring program are the field sampling and the laboratory analysis.

Soils are the only components routinely monitored at these sites. It is planned to integrate total monitoring efforts (i.e., vegetation, air quality, water quality, and soil) at selected sites in the near future. A concerted effort will be made to combine activities of the relevant provinces and federal agencies.

An initial assessment of the sensitivitiy of Alberta soils to acid deposition has been completed. Maps depicting (1) potential of soils and

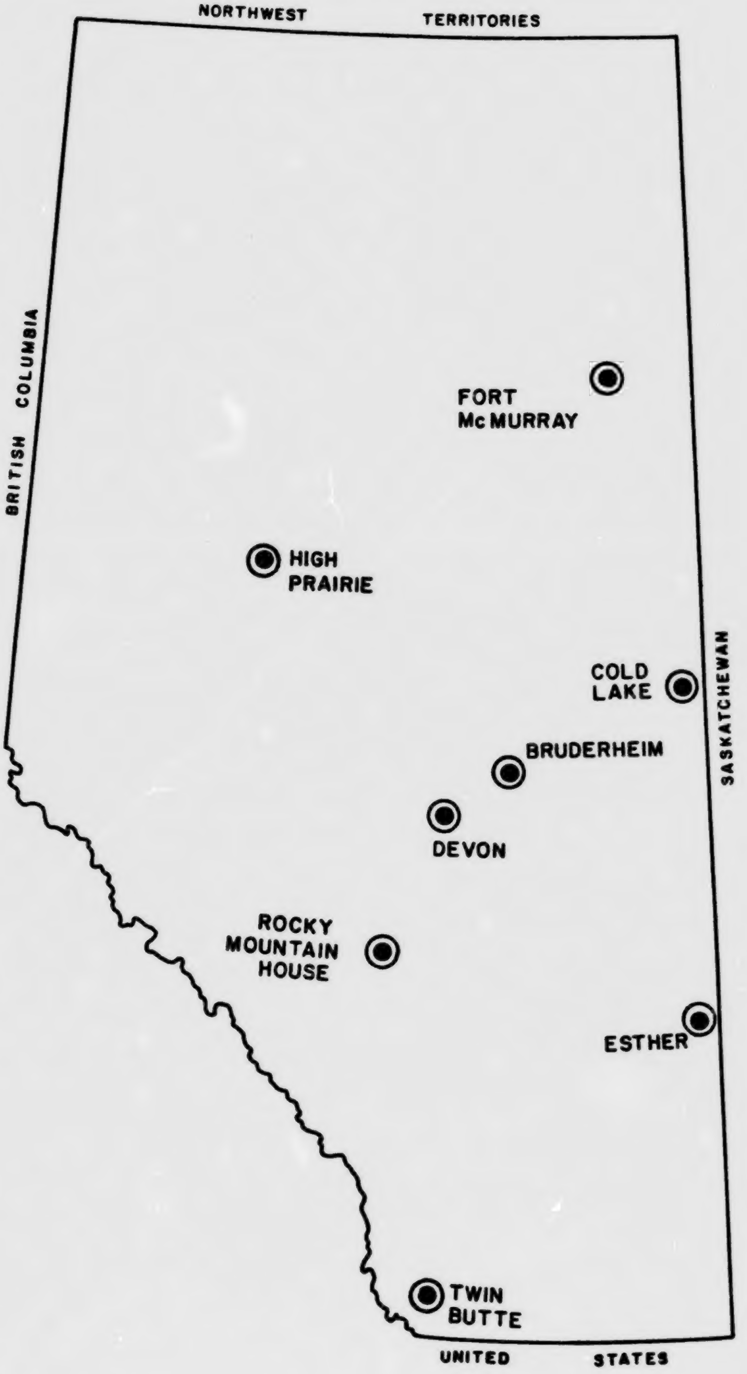


Figure 2. Long-term soil acidification monitoring sites.

geology to reduce acidity of incoming acid deposition, and (2) sensitivity of soils to acidic inputs have been prepared.

2.6.3.1 Field sampling. Five characteristics were considered important to the selection of monitoring sites:

1. General areas selected for sampling were those identified as areas receiving maximum amounts of acid deposition. These were areas downwind from major sour gas plants, oil sands plants, coal-fired generating plants and heavy oil extraction plants. Care was taken, however, to locate in areas beyond which the localized effects of elemental sulphur dusting could have been an additional source of acid deposition.
2. The most sensitive soils were sampled in each area.
3. Plot areas were located on sites that were as homogeneous as possible with regards to soil characteristics.
4. Undisturbed native soils were selected. Six of the areas are forested and two are on native grassland. Cultivated areas were excluded because of the potential for soil acidification from farm management practices (e.g., fertilizers).
5. Each sampling site was secured, along with a buffer area, by registration with the Land Titles Office. As a precautionary measure, paired plots were established at each site.

The first two characteristics were those considered essential factors for an early warning system. The next two characteristics are important to the detection of subtle changes. The final characteristic is essential to allow for long-term monitoring.

2.6.3.2 Laboratory analysis. Due to the many different effects of soil acidification, the laboratory analysis program is designed to measure changes in the status of a broad variety of soil chemical properties. Elements chosen for measurement include hydrogen, calcium, magnesium, potassium, sodium, aluminum, iron, manganese, sulphur, nitrogen, carbon, and phosphorus. Soil testing procedures were selected on the basis of being widely accepted and appropriate for measuring the properties of acidic soils. Particular care has also been taken to reduce the introduction of variability due to the laboratory analysis program.

2.6.4 Water Quality Monitoring

The Water Quality Control Branch of the Pollution Control Division maintains a fixed, long-term monitoring network on 11 river locations and four central Alberta lakes (Ethel, Baptiste, Nakamun, and Wabamun). All sites are sampled monthly, and analyzed for a wide range of chemical constituents and indicators of acidity.

An initial province-wide assessment of the sensitivity of Alberta lakes to acid deposition has been completed.

This analysis has identified a number of areas in the northern upland regions, the Canadian Shield area, and the Rocky Mountain National Parks which are potentially sensitive. Accordingly, our long-term monitoring network will be expanded to incorporate representative lakes in areas which may be subject to increased atmospheric loading of acid-forming substances. The expansion will occur in 1986 or 1987, subject to budgetary conditions.

3. ANIMAL HEALTH

The Alberta Environmental Centre is undertaking a study on the health effects of sulphur gases. The objective is to determine the effects of toxic or potentially toxic gases, vapours, particulates, and aerosols on animals and, by extrapolation, on humans. Current studies include the characterization of a 69 L inhalation exposure chamber, commissioning of a new 359 m^2 inhalation toxicology containment facility, studies on the acute toxicity of hydrogen sulphide, in vitro studies and techniques for evaluation of adverse effects of pneumotoxicants, and implementation of an inhalation exposure system using 2 m^3 exposure chambers, and field investigations of possible effects on livestock.

4. DEPARTMENTAL AIR QUALITY AND ENVIRONMENTAL CONTAMINANTS PROGRAM

The major emphasis of Alberta Environment's deposition research program has focussed primarily on the issue of 'acid rain'. However, the effect of other toxic pollutants/contaminants from natural and anthropogenic sources on health and the environment are of major concern provincially, nationally, and internationally. With our increasing population base and economic development, the increase in pollutant emissions and their secondary or tertiary reaction products are important contributors to the degradation of air quality. Further, today with nearly 50 000 chemicals utilized in Canada, it is impossible to escape exposure at some level to chemicals in the work place, at home, in the air, and in food products. Environmental contamination has been increasing steadily within this century. The primary concern is that although toxic pollutants and contaminants may be emitted and dispersed at low concentrations, they may persist and accumulate in the environment and bioaccumulate in the food chain. These contaminants impact the environment through industrial effluents/air emissions, spills, spray programs, and natural releases. Because of their potential impacts, Alberta Environment has developed research programs to address issues related to air quality and environmental contaminants.

4.1 AIR QUALITY

In recent public surveys in Alberta, air quality has been defined as a leading environmental concern; the issue ranked fourth in Alberta in 1981, and first in 1982 and 1983. The assessment and management of ambient air quality requires research and monitoring to understand the quantitative relationships among background air quality, emissions, ambient air quality, atmospheric transport/dispersion/diffusion, chemical transformation, deposition, and probable effects.

Specific objectives of the air quality program are:

1. Monitoring
    a. To characterize and quantify atmospheric pollutants from various sources;

   b. To quantify the contributions of local and regional sources to air quality degradation; and
   c. To determine short and long term trends in air quality.
2. Effects
   a. To develop methodologies to identify and predict environmental damage and health effects caused by atmospheric pollutants; and
   b. To determine the socio-economic impacts.
3. Management Strategies
   a. To determine what are the best possible management strategies and regulatory controls required to prevent or mitigate degradation of air quality.

Research in three high priority areas has been proposed.

4.1.1 Flaring

Historically, flares have been used in the oil, natural gas, refining, and petrochemical industries to dispose of gases in a safe manner. However, the efficiency of flaring in the disposal of reduced and oxidized sulphur compounds and other toxic compounds has been a concern for several years. Odour, smoke, air quality, and health problems in the vicinity of these industrial activities have been attributed to flaring operations. The real or perceived risks associated with these activities has given rise to environmental and health concerns which must be adequately addressed.

In 1986, a Government/Industry Consultative Committee on Flaring was established by Alberta Environment. Based on a review of relevant studies pertaining to flaring, the committee felt that further investigation was necessary to confirm and define more clearly the environmental and health impacts associated with flaring.

The first initiative identified by the committee was a two part study to document and compare the design and operating practices of flaring operations in Alberta against the technology available through suppliers and designers. These studies are being funded by the federal and provincial governments.

4.1.2 Fugitive and Uncontrolled Emissions

An area of growing concern is the environmental and health effects of fugitive and uncontrolled emissions. In most industrial operations, only the main source of pollutants are routinely monitored. However, all facets of heavy oil recovery and production operations are potential sources of atmospheric emissions which may adversely affect ambient air quality and the environment. These emissions have not been characterized or quantified. Although these emissions may be emitted and dispersed at low concentrations, they may persist and accumulate in the environment and food chain. Also nitrogen oxide and hydrocarbon emissions are precursors to photochemical oxidant pollution which can damage forest and agricultural ecosystems. A more quantitative assessment is needed if a thorough investigation and understanding of the effects is to be obtained. Information from the proposed research will be used to ascertain the need to and the appropriate way to control emissions to avoid undesirable effects.

4.1.3 Urban Air Quality

Urban air quality has been identified as a leading environmental concern. Studies have indicated that the potential for serious pollution problems exists in both Calgary and Edmonton, major urban centres in Alberta. The efficient management of urban air resources and the planning and design of environmental legislation, impact assessments, and land use planning requires a comprehensive air quality assessment. This necessitates an understanding of the quantitative relationships among urban emissions, background air quality, ambient concentrations, atmospheric transport/dispersion/diffusion, photochemical reactions, and probable effects. To facilitate the design of strategic and effective research, pertinent research undertaken in Alberta was reviewed and synthesized in the context of national and international activities. Recommendations for future research were provided. The following research has been carried out to address two of the recommendations:

1. An urban air quality model(s) was selected for application in Alberta for use as a research tool and for airshed management;

2. The development and design of a detailed, comprehensive research and monitoring protocol to: (a) characterize and quantify temporal and spatial variability in the chemical and physical properties of urban aerosols, and (b) determine the relationship between visibility and particle mass loading.

4.2 ENVIRONMENTAL CONTAMINANTS

To assist in the planning and management of contaminants, short term research initiatives will address the identification of, movement of, dose effects of, evaluation of, and possible management strategies for contaminants. Over the longer term, research will investigate the impact and response of ecosystems to contaminant exposure and develop effective monitoring and control strategies.

Current research related to deposition is being carried out in two main areas:

4.2.1 Oil Sand Extraction and Discharge

The transport, transformation and removal, persistence and accumulation of contaminants from the heavy oil recovery and processing industry is being examined using the concept of fugacity.

4.2.2 Decommissioning

Research is directed at ensuring the proper abandonment of industrial and municipal facilities. A phosphogypsum study will identify the environmental and health hazards associated with phosphogypsum tailings. It will also assist in the development of national guidelines for disposal of phosphogypsum wastes.

5. EMISSIONS CONTROL TECHNOLOGY

Concurrent with the above studies, work will be undertaken on control technologies to reduce emissions at their source. For some time now, the Alberta Environmental Centre has been involved in the assessment and development of a wide range of concepts/processes for the control of acid-forming emissions. Source industries such as gas processing, thermal power, oil sands, gas compressors, and waste incineration have been considered. The use of magnesium oxide to remove sulphur dioxide gas from a sour gas processing plant has been developed and successfully tested at bench-scale. A pilot-scale project is under consideration for funding jointly by Alberta Environment and Environment Canada.

Assuming that feasible control technologies will some day eliminate emissions, and emission sources in some areas may be decommissioned over the intervening period, important questions will be: does the ecosystem recover on its own and, if so, how fast? Where possible, research will be focussed on these questions using field measurements in areas as the opportunities present themselves.

6. PROGRAM FRAMEWORK AND MANAGEMENT STRUCTURE

Overall co-ordination for the Departmental Acid Deposition Research Program is provided by the Research Management Division with the advice and support of the Departmental Committee on Acid Deposition (DCAD). Membership on DCAD includes representatives from Pollution Control Division (PCD), Standards and Approvals Division (SAD), Earth Sciences Division (ESD), Alberta Environmental Centre (AEC), Research Management Division, and other staff from the department to address specific program needs. DCAD addresses all activities, including research, monitoring, and ensures liaison between the Departmental, W&NC-LRTAP, and Government/Industry Acid Deposition Programs. The objective of the liaison is to share technical knowledge and prevent duplication of efforts. To ensure that comparable, scientifically valid methodology is used in the Departmental program, Alberta Environment has access to the Scientific Advisory Board of Government/Industry Acid Deposition Research Program.

A new system for approving research projects has been instituted by the Department. Program Planning Committees have been set up to identify and prioritize research projects to address major environmental issues in the province. In the case of acid deposition, the DCAD, as one of its functions, fills the requirement for an acid deposition research program planning committee. Where appropriate, Departmental project objectives and methodologies will be reviewed by external scientists and their suggestions incorporated.

7. CONCLUSION

The Acid Deposition, Air Quality, and Environmental Contaminants Programs for Alberta Environment should be viewed as a multi-faceted program of research, monitoring, and liaison activities which are designed to address all concerns for the potential effects of atmospheric deposition in the province. It is likely that research and monitoring activities will continue well into the 1990s, as long as concerns of Albertans regarding environmental and air quality persist.

8. ACKNOWLEDGEMENTS

The authors wish to thank their colleagues in the division, Mr. C. Powter, Ms. S. L'Hirondelle, Mrs. P. Papirnik, and Mr. E. Baddaloo for their efforts on developing and administering the department program and for their assistance in preparing this paper.

Thanks also to Mr. D. Trew, Dr. C. Palmer, and Mr. A. Schulz for contributions to the drafting of the sections on the department's monitoring program.

A special thanks to my secretarial staff for typing the manuscript.

9. REFERENCES

Alberta. Department of the Environment. 1982. Symposium/Workshop proceedings: acid-forming emissions in Alberta and their ecological effects. Sponsored by Alberta Environment. Canadian Petroleum Association, and Oil Sands Environmental Study Group. 1982 March 09-12; Edmonton, Alberta. 648 pp.

Alberta Government/Industry Acid Deposition Research Program (ADRP). 1984. Researching acid deposition: workshop proposals. Canadian Petroleum Association. Calgary, Alberta. 59 pp.

Addison, P.A. 1980. Baseline condition of jack pine biomonitoring plots in the Athabasca Oil Sands area; 1976-1977. Prep. for Alberta Oil Sands Environmental Research Program by Northern Forest Research Centre, Canadian Forestry Service. AOSERP Report 98. 43 pp.

Hesslein, R.H. 1979. Lake acidification potential in the Alberta Oil Sands Environmental Research Program study area. Prep. for Alberta Oil Sands Environmental Research Program by Fisheries and Environment Canada, Freshwater Institute. AOSERP Report 71. 36 pp.

Hocking, P. and D. Reiter, eds. 1973. Proceedings of Alberta sulphur gas research workshop I. 1973 November 01; Edmonton, Alberta. 196 pp.

Holowaychuk, N. and J.D. Lindsay. 1982. Distribution and relative sensitivity to acidification of soils, Sand River area, Alberta. Prep. for Alberta Environment, Research Management Division and Canadian Petroleum Association by the Soil Department, Alberta Research Council. RMD Report 82/13. 93 pp.

LaRoi, George H. and M. Ostafichuk. 1982. Establishment and vegetational survey of 16 Pinus Banksiana-dominated permant plots for the Athabasca Oil Sands ecological monitoring project in 1981. Prep. for Alberta Environment, Research Management Division by University of Alberta, Department of Botany. RMD Report OF-34. 133 pp.

Legge, A.H., D.R. Jaques, G.W. Harvey, H.R. Krouse, H.M. Brown, E.C. Rhodes, M. Nosal, H.U. Schellhase, J. Mayo, A.P. Hartgerink, P.F. Lester, R.G. Amundson, and R.B. Walker. 1978. Sulphur gas emissions in the boreal forest: the West Whitecourt case study: final report. Prep. for Whitecourt Environmental Study Group and Alberta Environment, Research Secretariat by University of Calgary, Kananaskis Centre for Environmental Research. 615 pp.

Legge, A.H., E.M. van Zinderen Bakker, Jr., E. Peake, and D.C. Lindsay. 1980. The oxides of nitrogen and their interaction in the environment: a review. Prep. for Alberta Environment, Research Secretariat, and Canadian Petroleum Association by University of Calgary, Kananaskis Centre for Environmental Research. 169 pp.

MacDonald, W.R. and H.S. Sandhu, eds. 1975. Proceedings of Alberta sulphur gas research workshop II, 1975 January 16 to 17; Kananaskis, Alberta. Jointly sponsored by Alberta Environment, Research Secretariat, and University of Calgary, Kananaskis Centre for Environmental Research. 174 pp.

Malhotra, S.S., P.A. Addison, and A.A. Khan. 1980. Symptomology and threshold levels of air pollutant injury to vegetation, 1979-80. Prep. for Alberta Oil Sands Environmental Research Program by Northern Forest Research Centre, Canadian Forestry Service. AOSERP Report 109. 17 pp.

Nyborg, M., R.W. Parker, S. Takyi, and P. Yeung. 1985. Deposition of sulphur and its influence on soils in the AOSERP study area. Prep. for Alberta Environment, Research Management Division by Soils Department, University of Alberta. RMD Report L-86. 153 pp.

Sandhu, H.S. and M. Nyborg, eds. 1977. Proceedings of Alberta sulphur gas research workshop III. 1977 November 17 to 18; Edmonton, Alberta. 334 pp.

Sandhu, H.S., H.P. Sims, R.A. Hursey, W.R. MacDonald, and B.R. Hammond. 1980. Environmental sulphur research in Alberta: a review. Edmonton; Research Secretariat, Alberta Environment. 90 pp.

Sandhu, H.S. and L. Blower. 1986. Acid forming emissions in Alberta, Canada. Environmental Management. 19 pp.

Smith, S.B. 1981. Alberta Oil Sands Environmental Research Program 1975 to 1980: summary report. Prep. by Research Management Division and S.B. Smith Environmental Consultants Limited. AOSERP Report 118. 170 pp.

Technical Committee for the Long Range Transport of Atmospheric Pollutants in Western Canada LRTAP activities annual reports.

APPENDIX I

1. Proceedings of Alberta Sulphur Gas Research Workshop I. Edmonton, Alberta; 1973 November 01. (Hocking, P., et al. 1973)
2. Proceedings of Alberta Sulphur Gas Research Workshop II. Kananaskis, Alberta; 1975 January 16-17. (MacDonald, W.R., et al.)
3. Proceedings of Alberta Sulphur Gas Research Workshop III. Edmonton, Alberta; 1977 November 17-18. (Sandhu, H.S., et al.)
4. Symposium/Workshop Proceedings: Acid forming emissions in Alberta and their ecological effects. Edmonton, Alberta; 1982 March 9-12. (Alberta Department of the Environment, Canadian Petroleum Association and Oil Sands Environmental Study Group)
5. Research acid deposition: workshop proposals. Canadian Petroleum Association, Calgary, Alberta. (Alberta Government/Industry Acid Deposition Research Program (ADRP) 1984)
6. Western Canada LRTAP Technical Committee. 1981, 1982, 1983, 1984 annual reports. (Research Management Division, Alberta Department of the Environment, Edmonton, Alberta)
7. Alberta oil sands environmental research program 1975 to 1980: summary report. (Smith, S.B. 1981)
8. Environmental sulphur research in Alberta: a review. (Sandhu, H.S., et al. 1980)
9. The oxides of nitrogen and their interaction in the environment: a review. (Legge, A.H., et al. 1980)
10. Urban Air Quality Workshop. Edmonton, Alberta; October 1983
11. Urban Air Quality Research Needs in Alberta: A Literature Review and Synthesis of Available Information (RMD Report 85/33).

Multimedia analysis and assessment of environmental toxic and carcinogenic substances: The regulatory connection.

Ronald Harkov - Office of Science & Research, CN 409, New Jersey Department of Environmental Protection, Trenton, N.J. 08625

Abstract - Most toxic substance issues are multimedia in nature, but are managed within regulatory agencies as completely separate items. In New Jersey, the Office of Science & Research (OSR) has been involved in multimedia toxic substance assessments of air, water, food and soil contamination. These efforts have led to one of the best toxic substances inventories in the US, and perhaps the most far-reaching program of its kind at the state level. The research described in this report sets the foundation for development of an integrated toxic substances program. While volatile organic compounds (VOC) are used for illustration purposes, it is clear that multimedia analysis of human toxic substance exposures will be needed to develop cost-effective environmental solutions. To this end a new environmental health office is being initiated within OSR to address; risk assessment, risk reduction and risk communication aspects of a toxic substance regulatory program.

Introduction - The traditional segregation of pollution issues into water, air and solid wastes proved to be a workable arrangement, provided that the focus of each separate group was limited to media specific pollutants and/or pollutant measurements. Thus carbon monoxide is mostly an air pollution issue, while BOD or alkalinity are primarily water pollution issues. With the increasing emphasis on toxic and carcinogenic substances over the last 15 years, it has become clear that the traditional segregation of pollution issues does not allow for the intelligent development of sound regulatory programs.

In New Jersey (NJ), the Office of Science & Research (OSR) in the Department of Environmental Protection (DEP) has been conducting studies of toxic pollutants in ambient air, drinking water, industrial and sewage treatment plant effluents, contaminated fisheries, source emissions and other media (1-5). This information can be used to develop a unified approach for assessing toxic substances in NJ and for developing an overview for program integration within any environmental agency. To develop a comprehensive regulatory program for toxic substances accurate information is necessary in the following areas; pollutant sources, environmental levels, human exposures, health risks and mitigation methods. In addition, from our experience in NJ, one might consider a public communication program for all or some of these portions of a toxic substances regulatory program. Because OSR's primary focus has been on investigating toxic substances in the NJ environment, this paper will focus on pollutant sources, monitoring and human exposure efforts carried out in the state.

For the purpose of the present discussion, toxic and carcinogenic substances should be properly defined. In a review on airborne toxic pollutants, Goldstein (6) found it very difficult to develop an acceptable definition for these materials. In this paper, the definition of toxic and carcinogenic substances includes all those toxicants with the potential to cause human disease that are not currently subject to health based standards in the Clear Air Act of 1977 or the Safe Drinking Water Act of 1974. It should be emphasized that the development by US-EPA of the so-called priority pollutant list for water and the Pb standard in ambient air helped focus the scientific community's attention on toxic substances. The compounds provided in Table-1 are examples of toxic air pollutants and while this list identifies the major substances of concern, it is clear that we focus on a small percentage of the possible toxic substances in the air environment.

To reduce the discussion down to a manageable size, volatile organic compounds (VOC) will be the main subject for the remainder of this report. Volatile organic compounds can be defined as those organic substances with a vapor pressure greater than or equal to 0.02 psi at standard conditions. This class of pollutant includes; a) a number of human and/or animal carcinogens such as benzene or vinyl chloride (7), b) photochemically active precursors of smog components (8), c) common ground and surface water contaminants (9,10), and d) major components of industrial/commercial processes and consumer products (11,12).

Pollutant Sources - Information can be gathered on VOC sources utilizing both qualitative and quantitative approachs (13). Data on industrial/commercial usage of VOC is generally more available and of better reliability than emissions, effluent or waste disposal estimates. Likewise fuel usage information is a better qualitative indicator of losses to the environment than are estimates of emissions, leaking storage tanks, etc. For the toxic air pollutant projects carried out in NJ, Chemical and Engineering News Annual reports, the EPA's organic chemical producers data base, state air permit files, the industrial survey project (ISP) and fuel usage patterns were utilized to estimate the importance of various VOC sources to the air environment in the state (13,14). Currently, we are also conducting a limited number of combustion source emission tests for semi-volatile organic pollutants (SVOP) such as polycyclic aromatic hydrocarbons (PAH), nitro-PAH and PAH-quinones (15).

The NJ ISP provides a good example of how information on industrial emissions, discharges and waste disposal practices could be integrated into a comprehensive toxic substances program. The information on toluene shown in Figure-1 provides an indication of the distribution of industrial air emissions on a municipality basis in NJ. Also, industrial air emissions account for approximately 84% of the losses of this pollutant from this source category to the NJ environment. Obviously liquid fuel evaporative and combustion losses of toluene need to be factored into this assessment. With an understanding of the spatial distribution of VOC losses to the NJ environment, combined with environment fate and public health information, plausible hypotheses can be generated and investigated to fine tune assessing the significance of the various discharge vectors in a specific municipality. For example, it became clear from the ISP that significant quantities of VOC are discharged to publically owned treatment works (POTW's) in NJ. A subsequent investigation of a large, regional POTW in Middlesex County, indicated that these facilities are significant emissions sources for these materials (16). Considering that 75% of the industrial effluents in NJ are directed to POTW's (PC. Goldestein-NJPDES Program) and that VOC represent a significant portion of these discharges, serious attention by DEP is now being directed towards reducing VOC losses to the environment via this avenue. Such a pollutant reduction program would have multifaceted environmental benefits; a) a contribute to ozone control, b) reduce toxic substances levels in air, c) reduce the toxicity of POTW effluents and d) increase the options available for environmentally sound sewage sludge disposal.

It should be made clear that source information gathered from legally mandated surveys, such as statewide right-to-know programs, are inherently incomplete and not always accurate. Yet without information on pollution sources, a holistic toxic pollutant regulatory program cannot be developed.

Environmental Levels - Measurements of toxic pollutants are complex, costly and often imprecise (17, 19, 30). Concentration measurements in the environment provide an indication of; a) success of a regulatory program, b) influence of environmental fate on media-specific pollutant partitioning and c) can be used to approximate human exposures. Since toxic pollutants generally occur at low concentrations, large sample volumes, aggressive sample extraction, precise separation and specific/sensitive detection methods are necessary to carry out monitoring programs for environmental levels.

Various sampling strategies can be used to test or develop different hypotheses related to ambient concentrations of VOC and human health. In NJ, selected VOC have been monitored in the ambient air at urban and background sites, hazardous landfills, municipal landfills, industrial sites and at a POTW (16,21,24). These different studies help provide a prospective for where the greatest regulatory effort should be directed to minimize human exposure to these toxic substances via the air route. The information provided in Table-2 for four selected VOC indicates that localized, source specific problems need to be addressed prior to efforts with area sources. However, it was also discovered that small, localized VOC sources may be more important than large sources. For example during the NJ program on Airborne Toxic Elements and Organic Substances (ATEOS), a localized truck body manufacturer was identified as a major contributor to the peak toluene levels found at the Newark site (Figure -2), but not at the other two locales studied (25).

Investigations of potable water supplies in NJ indicate that certain VOC are found in both ground and surface waters (2, 10, 26). The most commonly found substances in groundwater, such as trichloroethylene or methylene chloride, are somewhat polar and are high use solvents. Significant localized groundwater degradation by VOC has been documented in NJ due to improper waste disposal practices, spills, leaking underground storage tanks and/or chemicals associated with septage tanks (9, 10, 27). Some trihalomethanes appear to be frequently found in certain finished potable water supplies subject to chlorination (26).

Information on food and indoor air pollution VOC levels have not been extensively documented in NJ. However, the initial results from the studies of personal exposures to selected VOC in Elizabeth and Bayonne, NJ (TEAM study) indicate that indoor levels may be significantly elevated over outdoor levels (28). Outside of serious concerns about the quality of the reported measurements, any subsequent verification of the TEAM study results poses an interesting dilemna for the regulatory community (29). At the very least regulatory programs will need to be coordinated between consumer product, occupational health and environmental protection agencies to achieve the greatest exposure reduction in the most cost effective manner. If selected VOC are associated with food precessing and packaging then perhaps this vector of exposure needs to be better documented. Limited information has been developed for VOC in food, thus substances such as ethylene dibromide, methylene chloride, chloroform and styrene have been found in food supplies (30).

Human exposures - The state-of-the-art for exposure assessment related to toxic substances has advanced significantly in the last 10 years (31). Different levels of assumptions are needed depending on the exposure assessment approach adopted by a regulatory agency. Recently, EPA adopted guidelines for conducting exposure assessments (32), while specific attention has been directed towards this issue in air pollution epidemiology (33). Modelling approachs for air, water and/or waste disposal scenarios which combine information on environmental fate provide the crudest estimates of human exposures. Such an approach was utilized for selected atmospheric toxic substances by EPA in the so-called Six Month Study (34).

The next level of sophistication in exposure assessment comes from combining environmental monitoring data, with time/activity patterns and assumptions on human physiological and internal partitioning factors. Such an effort has been carried out with perchloroethylene data collected during the ATEOS project (35). Utilizing the standard approach described by CAG (36), lung absorption patterns for perchloroethylene (37), time/activity patterns (38), and extrapolation from indoor/outdoor ratios of SO_2 (39), the exposure estimates are provided for three NJ locales (Table-3). While Wallace et al (28) found indoor/outdoor ratios for perchloroethylene of 2.2 from data collected in NJ homes, because of data quality issues associated with this study, we view the TEAM results with a measure of skepticism. Thus until the TEAM results are verified, we prefer to assume that perchloroethylene is primarily on outdoor pollutant. Burke (26) compared selected VOC exposures for individuals in NJ on the basis of ground or surface water use and atmospheric concentrations (Table 4-5). Although the assumptions made in the study cannot be completely justified, it is clear from this analysis that the air route of exposure is more often than not the greatest source of VOC exposures in NJ. From such an analysis, regulatory agencies could begin to develop more focused and cost effective pollution control programs in their respective jurisdictions.

Carrying our personal monitoring provides the most appropriate estimate of exposure based on our current understanding of this issue (40). Most personal monitoring for environmental contaminants have been based on single exposure vector pollutants (air), such as carbon monoxide or respirable particles (31). The information collected in NJ during the TEAM study included water samples (41) and thus this study added an additional level of sophistication to the exposure assessment field. Most toxic substances, including VOC, are found in air, water and food. Accurate personal monitoring studies must include the measurement of all three exposures vectors. This is particularly true since many toxic substances are either bioconcentrated in foods or are efficiently adsorbed by foods during processing, packaging, storage and preparation. A total human exposure study (THES) of benzo(a)pyrene (BaP) has been initiated in NJ. During the THES project, personal air, water, food and soil levels of BaP will be documented to develop a complete exposure picture for this carcinogenic pollutant (42). To the best of our knowledge, this modest effort represents the first attempt to address all major exposure routes for a toxic substance.

A new and very promising area for accurate exposure assessments is chemical and biochemical dosimetry (43). Harris (44) provides a good overview of the advantages and caveats associated with the utilization of DNA-adduct dosimetry. In essence this approach reduces all the exposure routes, environmental fate and human detoxification processes down to a single measure of exposure. While the formation of DNA-adducts appears to be an important step in the development of certain cancers, additional studies are necessary to evaluate whether DNA-adducts are good estimates of exposure and are accurate qualitative and/or quantitative indicators of disease (44). In the NJ THES project, we have proposed working with researchers at a major medical school to assess BaP-DNA-adducts in the blood of our test population (45). Although the THES project is limited in scope, the measurement of BaP-DNA-adducts and with corresponding air, water, food and soil exposure estimates, may provide the most tightly linked environmental toxic substance exposure study conducted to date.

Synthesis - The toxic substances program in OSR has led to the development and evolution of many key regulatory programs in NJ. Examples of some programs developed from OSR's efforts include those associated with hazardous site cleanup, drinking water, groundwater, toxic air pollutants and contaminated fisheries. As the questions being asked of our regulatory agency become more complex, these efforts need to become better integrated. A new health assessment program has been initiated in OSR and this program will have three major components: risk assessment, risk reduction and risk communication. In short, what is intended is to combine our environmental toxic substance investigation abilities with state-of-the-art health assessment, pollution abatement and public communication/participation programs, so that the DEP has the best possible tools to make sound regulatory decisions in the years ahead. This program is a great challenge; finding environmental problems is relatively easy, developing and implementing state-of-the-art solutions is much more difficult. Combining the best science, engineering and social science information will hopefully lead to cost-effective reductions in environment exposures to toxic substances in NJ.

Literature cited

1. Harkov R. 1983 Toxic air pollutants in NJ NJ Dept. of Env. Prot. 49 pp.
2. Tucker, R. 1981 Toxics in groundwater NJ Dept. of Env. Prot. 60 pp
3. McGeorge, L. et al 1983 Mutagenicity analysis of industrial effluents. NJ Dept. of Env. Prot. 38 pp.
4. Belton, T. et al 1983 PCB's in selected finfish caught within New Jersey waters. NJ Dept. of Env. Prot. 36 pp.
5. Harkov, R. et al 1986. A preliminary assessment of particulate phase organics measured in combustion source effluents. In prep.
6. Goldstein, B. 1983. JAPCA 33:454-467.
7. Harkov, R. 1982. STOTEN 26:67-85.
8. NAS 1977. Ozone and other photochemical oxidants National Academy of Sciences, Wash. D.C. 719 pp.
9. Clearey, R.W. et al 1985. Groundwater Pollution and Hydrology Princeton Assoc. Princeton, NY
10. NJDEP 1986. Results of initial testing for hazardous contaminants in public water supplies. NJ Dept. of Env. Prot. 32 pp.
11. Sheldon, L. S. et al. 1986. Volatile organic emissions from building materials. In, Prtc. 79th Annual APCA meeting, Minn, Minn. #86-52.3, 16 pp.
12. NAS 1981. The alklyl benzenes Nat. Acad. of Sci, Wash. D.C. 384 pp.
13. Harkov, R. and R. Fischer 1982. Development and initiation of an integrated monitoring program for toxic air pollutants. In, Proc 76th Ann APCA meeting, New Orlean, La. #82-11, 21 pp.
14. Harkov, R. and A. Greenberg 1985 JAPCA 35: 238-243.
15. Stevenson, E. et al. 1986. New Jersey Industrial Survey Final Report. NJ Dept. of Env. Prot. 87 pp.
16. Harkov, R. et al 1986. Volatile organic compounds in the ambient air near a large, regional sewage treatment plat in New Jersey, submitted to Water Pollution Control Federation Journal.
17. EPA/APCA 1986. Measuring toxic air pollutants. APCA Pub. VIP-7, 907 pp.
18. Johnson, T.R. and S.T. Penkala 1985. Quality Assurance in air pollution measurements. APCA Pub. TR-3, 850 pp.
19. Afheim, I. et al 1984. CRC Crit. Rev of Env. Cont. 14:91-150

20. Harkov, R. et al 1986. JAPCA 36:388-392.

21. Harkov, R. et al 1984. STOTEN 38:259-274

22. Harkov, R. et al 1985. JEHS 20:491-501

23. Jenks, J. et al 1986. Industrial emission impacts in the New Jersey Environment: Results from a study near a barrel and pail manufacturing plant. In, Measuring Toxic Air Pollutants, APCA Pub. VIP-7, 907 pp.

24. Jenks, J. et al 1986. Air quality in the vicinity of solid waste landfills in NJ. In prep.

25. Harkov, R. et al 1983. JAPCA 33:1177-1183.

26. Burke, T.A. 1984. Assessing human exposures in epidemiological studies of drinking water quality and cancer. PhD. Dissertation, Univ. Penn 175 pp.

27. Kaisigbach, H. and W. Althoff 1983. Groundwater 21:538-544.

28. Wallace, L.A. et al 1985. Atmos. Env. 19:1651-1661.

29. Andelman, J.A. 1985. Env. Health Persp. 62:313-318.

30. Kelsey, M.I. 1983. Monographs on organic air pollutants. NCI contract No. NO1-CP-2600401, 638 pp.

31. Ott, W.R. 1985. Env. Sci. Tech. 19:880-886.

32. FR 1986. Guidelines for exposures assessment. Fed. Reg. 51:34042-34054.

33. NAS 1985. Epidemiology and air pollution. Nat. Acad of Sci. Wash., D.C., 224 pp.

34. Haemisegger, E. et al 1985. The air toxics problem in the U.S.: An analysis of the cancer risk for selected pollutants. EPA 450/1-85-001. 105 pp.

35. Harkov, R. 1986. The New Jersey ATEOS project: An overview of its importance and health/regulatory implications. In, Toxic Air Pollutants. eds, P.J. Lioy and J.M. Daisey Lewis Pub. In press.

36. CAG 1980. Carcinogen Assessment Groups method for determining the unit risk estimate for air pollutants. Unpublished EPA report 17 pp.

37. Monster, A.C. et al 1979. IACEH 42:311

38. Dockey, D.W. and J.D. Spengler 1981. JAPCA 31:153

39. Spengler, J.D. et al 1979. Env. Sci. Tech 12:1276.

40. Mage, D.T. 1985. Statistical relationships between exposure and dose. In, Quality Assurance in air pollution measurements, eds. T.R. Johnson, and S.J. Penkala, APCA Pub.-TR-3, 850 pp.

41. Wallace, L.A. 1986. An overview of the total exposure assessment methodology study. Vol. I Draft U.S. EPA Report 198 pp.

42. Harkov, R. et al 1986. Design of a total exposure study for benzo(a)pyrene in NJ: The microenvironmental study. In prep

43. Wogan, G.N. and N.J. Gorelick 1985. Env. Health Resp. 62:5-18.

44. Harris, C.C. 1985. Env. Health Resp. 62:185-192.

45. Santella, R.M. et al. 1985. Env. Health Resp. 62:95-101.

46. Harkov, R. et al 1981. Toxic and carcinogenic pollutants in NJ: Volatile Organic Substances. In, Proc. Toxic Air Cont., APCA Pub. 245 pp.

TABLE 1

Examples of Toxic Air Pollutants

Particles		Gases
Organic	Inorganic	
PAH	soot	halogenated hydrocarbons
Pesticides	asbestos	aromatics
PCB's	silicates	aldehydes
TCDD	trace metals	ketones
phthalates	radionuclides	nitrosamines
carboxylic acids	sulfate	epoxides
thiophenes	nitrate	ethers
aromatic amines		lactones
epoxides		nitroalkanes

From Harkov (7)

TABLE 2

Comparison of Mean Ambient Concentrations of Four Selected VOC at Various Monitoring Locales in New Jersey (ppbv)

	Site Description				
Pollutant	Batsto[46] Rural Site	Newark[21] Urban/ Industrial Site	Edgeboro[22] MSW Landfill	Kramer[22] Superfund Site	MCUA[16] Grit/Screen Area-POTW
Benzene	0.61	2.61	3.33	7.51	9.9
Toluene	0.59	4.93	27.8	46.5	88.7
Trichlor-oethylene	0.08	0.59	0.32	2.43	2.4
perchloro-ethylene	0.04	0.46	1.42	1.91	3.9
N=	42	39	15	15	15

TABLE 3

Exposure Estimates for Perchloroethylene from the ATEOS Program

Communities	Annual (mg/kg/day)
Camden	0.178×10^{-4}
Newark	0.280×10^{-4}
Elizabeth	0.262×10^{-4}

From Harkov (35)

TABLE 4

Comparison of Daily Exposure Levels of Six Common Pollutants in Drinking Water and Air

	Geo Mean Concentration		Daily Exposure(a)		% of Total Exposure	
Compound	Air	Water	Air	Water	Air	Water
			Surface Water Consumers			
Methylene chloride	2.30	2.34	46.00	4.68	91%	9%
Chloroform	.63	21.47	12.60	42.94	23	77
Trichloroethylene	2.16	1.91	43.20	3.82	92	8
Tetrachloroethylene	2.49	.04	49.80	.08	100	0
Benzene	5.62	5.73	112.40	11.46	91	9
Toluene	12.65	16.45	253.00	32.90	88	12
Total			517.00	95.88	84	16
			Ground Water Consumers			
Methylene chloride	2.30	27.32	6.00	54.64	46	54
Chloroform	.63	3.48	12.60	6.96	64	36
Trichloroethylene	2.16	9.61	43.20	19.22	69	31
Tetrachloroethylene	2.49	4.48	49.80	8.96	85	15
Benzene	5.62	4.45	112.40	8.90	93	7
Toluene	12.65	7.72	253.00	15.44	94	6
Total			517.00	114.12	82	18

(a) Assumes daily consumption of 2 liters of water and 20 cubic meters of air.

Note: Air measured in ug/cubic meter; water in ug/liter.

From Burke (26)

TABLE 5

Comparison of Daily Exposure Levels from Drinking Water and Air in Three New Jersey Cities

Compound	Geo Mean Concentration		Daily Exposure(a)		% of Total Exposure	
	Air	Water	Air	Water	Air	
			Camden			
Methylene chloride	3.50	2233.00	20.00	4466.0	2%	98%
Chloroform	.61	.90	12.20	1.8	87	13
Trichloroethylene	1.45	14.25	29.00	28.5	50	50
Tetrachloroethylene	1.87	9.10	37.40	18.2	67	33
Benzene	5.57	0.00	111.40	0.0	100	0
Toluene	9.41	0.00	188.20	0.0	100	0
Total			448.20	4514.5	9	91
			Elizabeth			
Methylene chloride	1.72	20.55	34.4	41.10	46	54
Chloroform	.53	62.93	10.6	125.86	8	92
Trichloroethylene	3.08	0.00	61.6	0.00	100	0
Tetrachloroethylene	2.95	0.00	59.0	0.00	100	0
Benzene	5.14	0.00	102.8	0.00	100	0
Toluene	16.63	0.00	332.6	0.00	100	0
Total			601.0	166.96	78	22
			Newark			
Methylene chloride	2.03	0.00	40.6	0.0	100	0
Chloroform	.87	40.95	17.4	81.9	18	82
Trichloroethylene	2.24	0.00	44.8	0.0	100	0
Tetrachloroethylene	2.81	0.00	56.2	0.0	100	0
Benzene	6.20	9.00	124.0	18.0	87	13
Toluene	12.93	67.45	258.6	134.9	66	34
Total			541.6	234.8	70	30

(a) Assumes daily consumption of 2 liters of water and 20 cubic meters of air.

Note: Air is measured in ug/cubic meter; water is measured in ug/liter.

From Burke (26)

Figure 1 Municipality based toluene air releases from industrial sources in New Jersey (Steveson et al 15).

Figure 2 Daily toluene variations at four New Jersey sites during the summer of 1981 (Harkov et al 25).

TOLUENE

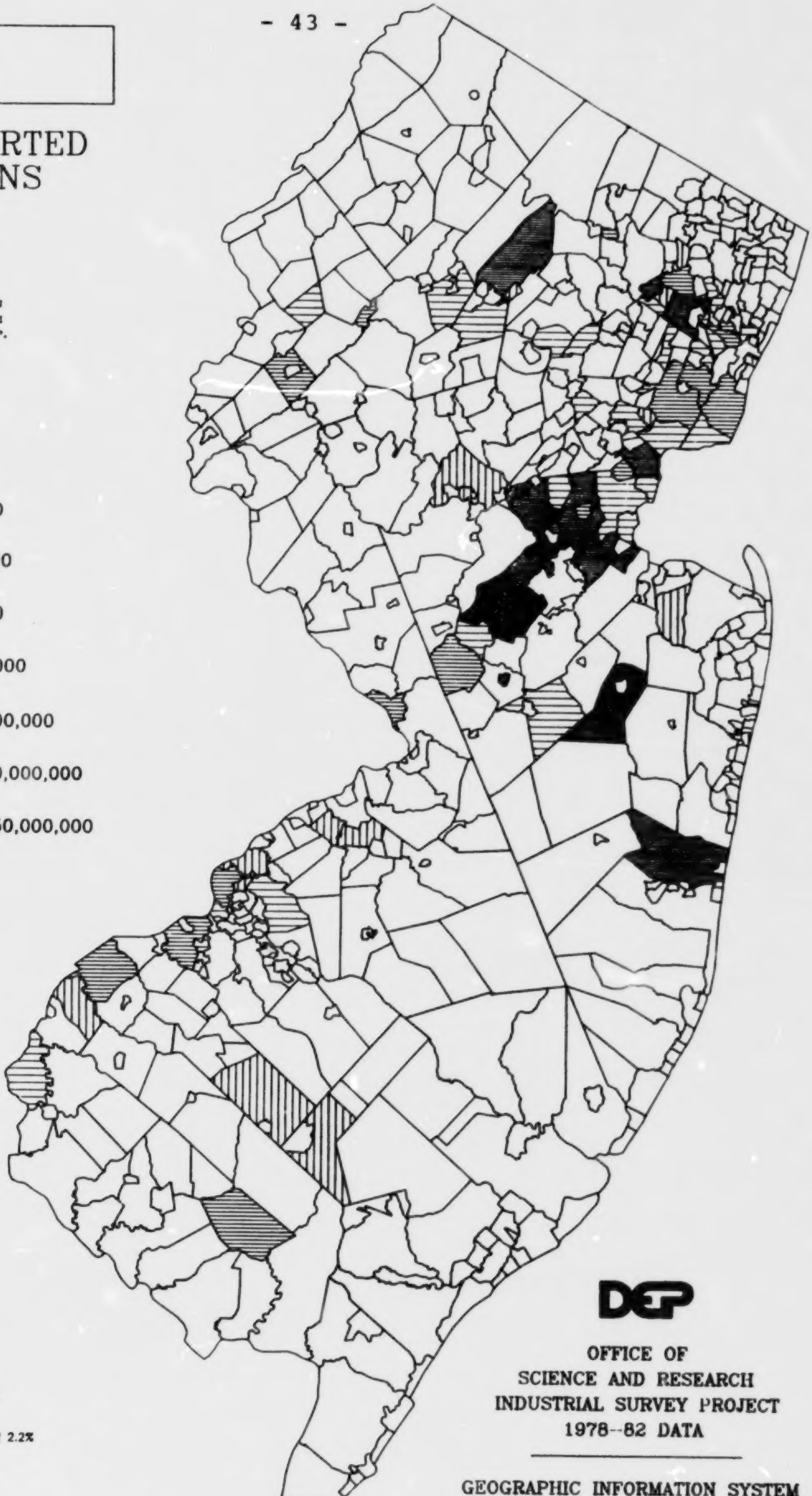
TOTAL REPORTED AIR EMISSIONS

BY MUNICIPALITY

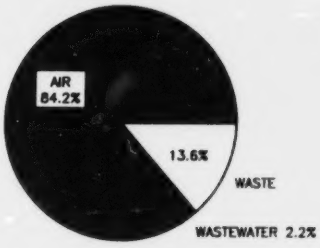
This map illustrates levels of the chemical reported in one environmental parameter. It is not intended to show exposure levels.

POUNDS

- □ NONE REPORTED
- ▥ LESS THAN 1,000
- ▤ 1,000 TO 10,000
- ▤ 10,000 TO 100,000
- ▦ 100,000 TO 1,000,000
- ■ 1,000,000 TO 10,000,000
- ■ 10,000,000 TO 50,000,000



TOLUENE
ENVIRONMENTAL
RELEASES

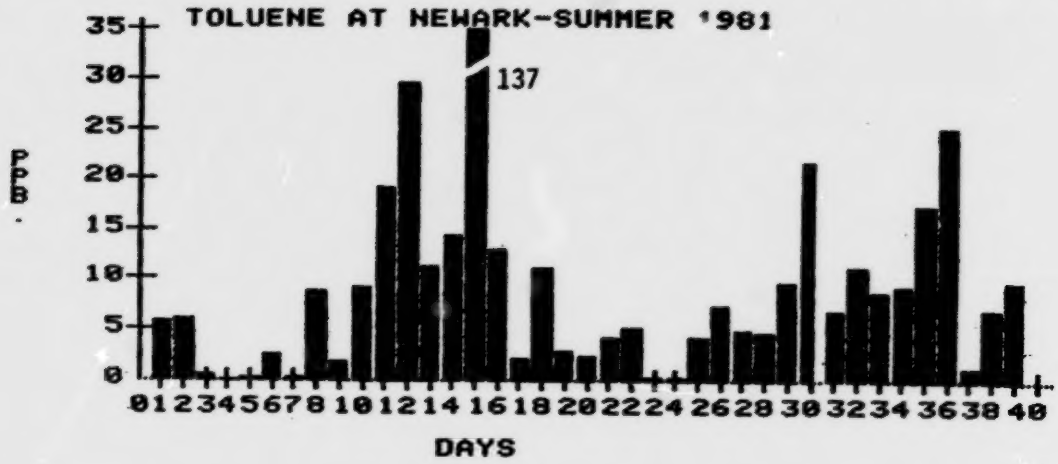


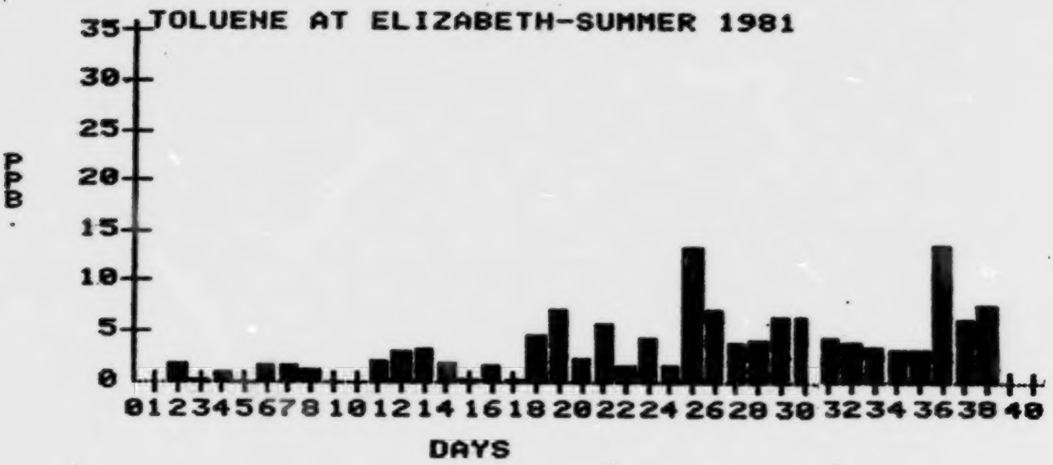
TOTAL RELEASE = 38703000 POUNDS

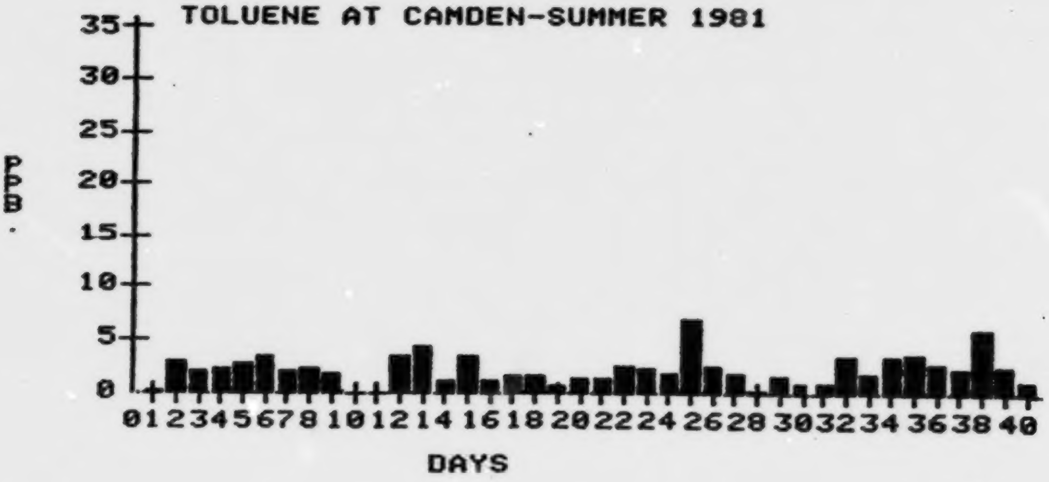
DEP

OFFICE OF
SCIENCE AND RESEARCH
INDUSTRIAL SURVEY PROJECT
1978--82 DATA

GEOGRAPHIC INFORMATION SYSTEM


TOLUENE AT NEWARK-SUMMER '981
137
PPB.
35
30
25
20
15
10
5
0
0 1 2 3 4 5 6 7 8 10 12 14 16 18 20 22 24 26 28 30 32 34 36 38 40
DAYS


TOLUENE AT ELIZABETH-SUMMER 1981
PPB.
35
30
25
20
15
10
5
0
0 1 2 3 4 5 6 7 8 10 12 14 16 18 20 22 24 26 28 30 32 34 36 38 40
DAYS


TOLUENE AT CAMDEN-SUMMER 1981
PPB.
35
30
25
20
15
10
5
0
0 1 2 3 4 5 6 7 8 10 12 14 16 18 20 22 24 26 28 30 32 34 36 38 40
DAYS

THE DEVELOPMENT OF TECHNIQUES FOR THE RAPID SCREENING OF MUNICIPAL REFUSE INCINERATOR FLY-ASH AND STACK GAS FOR PCDD/PCDF USING A TRANSPORTABLE TANDEM MASS SPECTROMETER (GC/MS/MS) SYSTEM

B. Shushan and A. Ngo., SCIEX®, Thornhill, Ontario
V. Ozvacic, G. Wong, G. DeBrou, B. Bobbie, and R.E. Clement,
Ontario Ministry of the Environment, Toronto, Ontario
B. Chittum, Wellington Environmental Consultants, Guelph, Ontario
S. Thorndyke, Ontario Research Foundation, Mississauga, Ontario

1.0 FLY-ASH

1.1 INTRODUCTION

The incineration of municipal refuse for the purposes of energy recovery has been linked to the production of undesirable byproducts notably polychlorinated-dioxins and -dibenzofurans (PCDD/PCDF). Since these substances are found in incinerator stack gases and fly-ash in miniscule amounts, methods for the analysis of these trace chemicals must therefore be sensitive and selective. This is currently accomplished by time and resource consuming wet chemical clean-up steps followed by gas chromatography mass spectrometric (GC/MS) analysis. The goal of obviating the time and resource consuming clean-up stages by using more specific analytical methods is a desirable one, since much of the cost for such sample analyses is in these clean-up stages. Furthermore, if analyses could be performed more cheaply and faster, more information could be gained which would lead to a better understanding of the processes involved in the formation of substances like PCDD/PCDF during incineration.

The goals of the present work were to investigate GC/MS/MS analysis of rapidly derived extracts of municipal refuse incinerator fly-ash. Tandem mass spectrometry (MS/MS) has demonstrated high specificity for the analysis of trace substances and, since its introduction of the world's first commercially available tandem triple quadrupole MS/MS system, SCIEX® has been involved in investigating novel ways of applying this new technology to solve problems in trace chemical analysis more rapidly. This type of development work has been carried out by SCIEX® in the past for the analysis of tetrachlorodibenzodioxin (TCDD) in soils under contract with the US-EPA (Region VII) and for the detection of polychlorinated biphenyls (PCBs) in stack gases under contract with MOE for example.

The scope of work performed by SCIEX® in this study was to:

(i) Develop a rapid "jar"-extraction* method for municipal refuse incinerator fly-ash which: (a) has the highest possible relative extraction efficiencies, (b) requires minimum sample handling, and (c) is amenable to GC/MS/MS analysis;

(ii) Determine whether crude (i.e. rapidly derived) fly-ash extracts exhibit interferences during GC/MS/MS analysis;

(iii) Compare "jar"-extraction efficiencies with those of conventional (Soxhlet) extraction methods using a variety of fly-ash types; and

(iv) Determine the reproducibility of the procedure.

1.2 EXPERIMENTAL

Three types of fly-ash samples were used in this development program: types C (Commissioner Street), A (Ashbridge Bay) and S (SWARU). Jar-extract method development was carried out using a sample of well characterised fly-ash of type C supplied to SCIEX® by MOE-LSB. This was used to ascertain which solvent systems supplied the best relative extraction efficiencies. The absolute extraction efficiencies would be tested by comparing jar-extracts to extracts derived by conventional 18h Soxhlet extraction methods. The conventional extracts were supplied by MOE-LSB and the other contract laboratory (Wellington Environmental Consultants (WEC)) involved in this study.

An extracting solvent comprising 2 parts toluene and 1 part methanol was found to provide relatively good extraction efficiencies for the majority of PCDD/PCDF congeners. A flow chart for the jar-extraction procedure can be found in last year's proceedings of this conference.

The tandem mass spectrometer used in the present work was the TAGA® 6000E tandem triple quadrupole MS/MS system manufactured by SCIEX®. A GC is directly coupled to the MS/MS system's ion source for sample introduction. The ion source is a Glow Discharge ion source at 200°C which uses Zero Air as the reagent gas at 35 ml/min flow providing a source pressure of some 1 Torr. The N_2/O_2 reagent gas mixture provides an efficient charge transfer medium for the ionization of aromatic hydrocarbons such as PCDD/PCDF while the oxygen acts in a cleansing fashion keeping ion source parts clean by "burning" off carbon deposits. Thus, crude extracts can be analyzed without having to clean the ion source after use. The discharge current was 1.2 mA and the molecular ions created in the source and selected by Quadrupole 1 (the first mass spectrometer) were fragmented in the quadrupole collision cell (Quad 2) by 65 eV collisions with Argon at 4 x 14^{14} atoms/cm^2 target gas thickness (see Schematic Figure 1). Daughter ions, specific to PCDD/PCDF are mass selected in Quadrupole 3 and detected by pulse counting. The GC conditions and a summary of GC/MS/MS analytical conditions can be found in last year's proceedings. The ^{13}C-PCDD/PCDF labelled components were added in the jar-extraction procedure in known amounts and act as internal standards for quantitation purposes. GC/MS/MS data were acquired 6.5 minutes into the GC run after injection of the crude jar extract. There were 7 groups of Q1/Q3 parent ion/daughter ion pairs covering the whole range of PCDD/PCDF congeners and the isotopically labelled internal standards. The quadrupole mass spectrometer settings and all other instrumental parameters are under computer control. The times for switching ion sets were determined by injection of a previously analysed fly-ash extract. This type of GC/MS/MS analytical procedure is termed multiple reaction monitoring (MRM) since the instrument is detecting the products of collisionally activated decomposition (CAD) ion-molecular reactions occurring between the mass resolving quadrupoles. The detection limits for the GC/MS/MS system were found to be in the sub picogram (pg) to 3 pg range for the injection of PCDD/PCDF standards.

---

* The term "jar"-extraction means simply a method of extraction requiring only the mixing of the matrix (fly-ash) with a suitable extracting solvent and mixing prior to analysis.

1.3 RESULTS AND DISCUSSION

The jar-extraction efficiencies were compared to conventional extraction methods for fly-ash sample C1 and the result is shown in Figures 2 and 3. The relative extraction efficiency was reasonably good for the lower chlorinated congeners but dropped off rapidly as the degree of chlorination increased.

The reproducibility of the techniques was demonstrated by analysing three C4 jar-extracts. The results are summarized in Figures 4 and 5 and demonstrate an average standard deviation of about ±10%.

In addition to the test of analytical reproducibility, QA/QC samples, comprised of crude and cleaned-up extracts of C1 and S1 fly-ash samples (derived by conventional extraction methods and furnished by MOE-LSB and WEC respectively) were analysed by GC/MS/MS and the results compared (see last year's proceedings and Figures 6 and 7).

The levels of PCDD/PCDF between crude and cleaned-up conventional fly-ash extracts shown in these figures indicate that both the other participating laboratories (MOE-LSB and WEC) produced extracts comprising comparable levels of PCDD/PCDF even though their degree of clean-up was substantially different, i.e. as per our QC/QC protocol MOE-LSB supplied a crude extract (no clean-up) while WEC supplied an extract which was taken through an extensive clean-up procedure. The fact that the GC/MS/MS results showed comparable levels for both crude and cleaned-up extracts indicates that the GC/MS/MS analytical technique is unperturbed by the other chemical constituents which make up the bulk of the fly-ash matrix. Furthermore, the results obtained by GC/MS/MS compared favourably with those obtained by GC/MS on the cleaned-up extract, establishing equivalency between the two analytical techniques.

1.4 CONCLUSIONS

The jar-extraction procedure followed by GC/MS/MS analysis is a rapid technique for the determination of PCDD/PCDF in fly-ash requiring less than 2 hours per sample. Although the reproducibility is within reasonable limits (± 9-11%) the extraction efficiencies were lower than those of conventional methods. The extraction efficiencies were found to be inversely proportional to the degree of chlorination and ranged from 75% for dichloro- congeners to 24% for octachloro- congeners. Not all fly-ash samples were amenable to the jar-extraction procedure. Type S fly-ash exhibited much lower extraction efficiencies and was, upon visual inspection, higher in carbon content. The crude C- and S-type extracts derived by conventional extraction exhibited no significant interferences when run by GC/MS/MS which bodes well for eliminating clean-up steps. Furthermore, the fact that the TAGA® 6000E MS/MS system is capable of transport within a mobile laboratory makes the jar-extraction GC/MS/MS analytical scenario amenable to on-site determinations of PCDD/PCDF at their source of production.

2.0 STACK GAS

2.1 INTRODUCTION

This portion of the paper is a brief account of the development of procedures for analysis of modified MM-5 stack gas sampling trains for quantities of PCDD/PCDF using GC/MS/MS. For this study a parallel analysis of the same stack gas using unmodified MM-5 sampling trains and GC/MS was undertaken. The goals of this section were to: (1) determine whether quantities of PCDD/PCDF are sufficiently high in municipal incinerator stack gas to permit a rapid GC/MS/MS analysis of crude XAD-2 resin extracts; (2) ascertain which fraction of total PCDD/PCDF is transmitted through the sampling train to the XAD-2 resin; and (3) assess whether the XAD-2 resin or the organics in the stack gas pose matrix problems for the GC/MS/MS analytical procedure when the XAD-2 resin is jar-extracted and the extract analyzed without cleanup stages.

The ultimate goal of the present work is to determine if the methods explored in this study can be practically implemented at the incinerator site in a mobile laboratory, outfitted with a transportable GC/MS/MS analytical system and rudimentary wet-laboratory facility. Accordingly, an attempt has been made to keep all sample handling and work-up methods as simple and as rapid as possible.

Stack sampling was done using parallel trains (modified MM-5 [see below] and unmodified MM-5) using XAD-2 as the sorbent resin to trap organics, including PCDD/PCDF. A smaller sorbent cartridge - one which contained 20 g of XAD-2 resin instead of the 100 g normally used - was the only difference between the modified and unmodified MM-5 trains. A schematic of the modified stack gas sampling "cartridge" is shown in Figure 8. About 2m^3 of stack gas were drawn through both trains' cartridges after passing through heated probe (P), particulate filter (PF), and filter bottom and connector (FBC). The modified MM-5 train cartridge contained two 10 g portions of XAD-2 resin separated by a glass wool partition. In both trains, stack gas and condensed water flow through the XAD resin and organics are adsorbed onto the sorbent material. In the modified cartridge the top 10 g resin portion adsorbs the organics and the bottom portion is used to recover any breakthrough.

The stacks were sampled isokinetically for approximately 180 min/run and sampling line temperatures were maintained at 125°C. The ends of the two parallel sampling probes were situated close to each other in the stack, and an equal volume (ca. 2 m^3) of stack gas drawn through each of the respective trains. Two incinerators were tested: a municipal refuse incinerator (MRI) (Commissioner Street) and a sewage sludge incinerator (SSI) (Ashbridge Bay). The MRI had a stack temperature of ca. 225°C and a flow of ca. 78 Nm^3/sec, and the SSI, a stack gas temperature of ca. 35°C and a flow of ca. 36 Nm^3/sec.

Prior to the GC/MS/MS analysis, the upper XAD-2 resin portion was subjected to the following analytical procedure:

1) Water was removed from the cartridge by first flushing with methanol, followed by purging with UHP Nitrogen at room temperature.

2) The top XAD-2 portion was emptied into a clean 50 ml centrifuge tube (see Figure 9) and spiked with 20 ul of a solution of ISI-200, the stock solution of isotopically labelled internal standards.

3) 4 X 5 ml aliquots of toluene were poured through the empty glass condenser/cartridge and collected in a graduated cylinder. The level of toluene in the cylinder was brought to 20.0 ml and transfered to the centrifuge tube containing the XAD-2 resin.

4) The centrifuge tube containing XAD resin and solvent was then vortexed (30 sec), and placed in an ultrasonic bath for ca. 0.5 hours.

5) A glass tube with a frit near the bottom was inserted into the centrifuge tube (see Figure 9) and the mixture centrifuged for 10 minutes forcing toluene through the frit and up the tube.

6) A 5 ml aliquot of toluene was then removed from the glass tube, and blown down to dryness and taken up with 5 ul solvent (toluene).

7) Depending on the levels of matrix and PCDD/PCDF, these solutions were diluted before being analyzed directly by GC/MS/MS.

All method development for the above "jar"-extraction procedure was carried out using the first two MRI samples. Altogether there were 5

MRI and 4 SSI samples run by GC/MS/MS and GC/MS. After stack sampling, the probe, and filter bottom connector from the unmodified MM-5 train were rinsed with solvent and analyzed by GC/MS after multi-column clean-up steps. The XAD-2 resin was extracted and analyzed by GC/MS using standard protocols[1] incorporating multi-column clean-up steps and isotopically labelled internal standards for quantitation. The GC/MS analysis results comprised two sets of data: quantities of PCDD/PCDF in (1) the probe and filter container; and (2) the condensor and XAD-2 resin. All GC/MS analyses were performed on cleaned-up extracts while GC/MS/MS analyses were performed on the rapidly derived crude jar extracts.

Prior to analysis of the modified MM-5 train samples by GC/MS/MS, a jar-extraction method development using clean XAD-2 resin indicated quantitative removal of test compounds OCDD and 1,2,3,4-TCDD from the resin employing MeOH/toluene mixtures which were as low as 20% in toluene. It was discovered during the analysis of the first stack gas sample that once XAD-2 resin is exposed to $2m^3$ of stack gas and condensate, it does not behave like the original material. In fact, it was necessary to use 100% toluene to ensure quantitative extraction of PCDD/PCDF from the used XAD-2. Treatment of the XAD-2 resin with MeOH while still in the cartridge provided an effective way of removing residual water prior to toluene extraction. When drawn through the cartridge by suction, methanol does not disturb the organic matter adsorbed onto the XAD-2 resins.

It was suspected that the analysis of crude XAD-2 extracts may demonstrate large mass spectral interferences due to the high organic content of the stack gas and that of the degraded XAD-2 resin after treatment with stack gas condensate. It is clear from Figure 10 that MS/MS provides sufficient specificity to overcome mass spectral interferences arising from the chemical matrix for tetrachloro- congeners. The two chromatograms shown in this figure are those of TCDD congeners analyzed by GC/MS/MS (m/z 320 fragmenting to m/z 259). The top chromatogram is that of a jar extract of fly-ash and the bottom that of a jar extract of XAD-2 resin, each run without clean-up. The isomer distribution for the two samples are almost identifical indicating that neither the XAD-2 resin, nor the extraneous organic matter in the stack gas, interferes in the MS/MS detection of TCDD. It is interesting to note that each of these samples came from the same incinerator except that the fly-ash was obtained and analyzed several months prior to the stack gas sample.

Unfortunately, one source of matrix interference not related to the tandem mass spectrometer analyzer was encountered for some MRI and all SSI stack gas samples. This non-mass spectral interference was due to a titration of the ionizing capacity of the chemical ionization ion source by the chemical matrix. The very large amount of neutrals coming from the GC column and passing through the ionization region is responsible for this effect. Such an interference leads to a complete suppression of response where even the isotopically labelled internal standards added to the crude extract are unobserved. Such an unfortunate result is understandable since the XAD-2 resin was observed to be very brown and discoloured with organic contamination after sampling. Furthermore, concentrated jar extracts of this resin looked more like a crude oily sludge than a solvent extract. The jar extracts from SSI stack gas appeared even dirtier than those from the MRI.

2.2 RESULTS & DISCUSSION

The levels of PCDD/PCDF from the MRI were enough to obtain good signal-to-noise for both GC/MS and GC/MS/MS analysis protocols. Figure 11 demonstrates the levels of PCDD and PCDF broken down into congener groups for the MRI samples. The average total PCDF and PCDD levels emanating from stack were 7,303 ng/m^3 (or 2 gm/hr) and 867 ng/m^3 (or 0.25 gm/hr) respectively. The highest levels were in the tetra- and penta- chlorinated congener groups. Although the mechanisms of dioxin and furan formation in the MRI are not well understood, the fact that PCDF are at higher levels than PCDD suggests that chlorinated dibenzofuran precursor's (e.g. PCBs) are higher in the feed stock than are chlorinated dioxin precursors (e.g. chlorinated phenols). Figure 12 is that of PCDD/PCDF levels found in SSI stack gas. Immediately one can see that PCDD/PCDF levels are considerably lower in SSI than in MRI stack gas especially in the tetra- and penta- chlorinated congener groups. The average levels observed are 1,265 ng/m^3 (or 0.2 gm/hr) for PCDD and 235 ng/m^3 (or 0.03 gm/hr) for PCDF, where the highest levels are those for the lower chlorinated congeners, especially dichlorodibenzo-p-dioxins (D_2CDD). This propensity toward lower chlorinated species in SSI stack gas may be a function of the lower stack gas temperatures where higher chlorinated constituents are precipitated out in scrubbing or cooling stages prior to entering the stack.

When we looked more closely at the distribution of PCDD/PCDF throughout the sampling train it was discovered that a good fraction was found in areas other than the XAD-2 cartridge. Figure 13 shows the partitioning of PCDF between the probe portion of the train and the XAD-2 condenser/ trap portion (so called "Probe" and "Trap" respectively). It is apparent that most of the PCDF is found in the trap, however, a significant amount is in the probe portion of the train. For the PCDD there are almost equal amounts in the probe and trap portions of the train (see Figure 14). Furthermore, under more careful scrutiny, the inter-congener and inter-run partitioning varies considerably (see Figure 15). There is, however, a general trend; i.e. with the exception of one of the runs, when going to higher chlorinated congeners, there are proportionally more PCDD/ PCDF found in the probe than in the trap. Thus, for tetrachlorinated congeners, there is 2 to 5 times the amount of T_4CDD and T_4CDF in the Trap than in the Probe, whereas for octachlorinated species, there is anywhere from 2 to 6 times the amount of material in the Probe than in the Trap.

This result is rather disappointing since, when we proposed this research, it was hoped that most of the vapour phase PCDD/PCDF would have made it through the sampling train to the XAD-2 cartridge. This, more than any other finding, leads to serious doubts that a rapid method of accurately determining PCDD/PCDF in municipal refuse incinerator stack gas can be accomplished using any analytical technique, as long as the transport of PCDD/PCDF through the sampling train shows these variable and low transport efficiencies.

In all cases, the MS/MS detector showed little interference to the XAD-2 and stack gas matrix however the shear amount of organic matter in these crude extracts had a deleterious effect on the ionizing capacity of the ion source in some of the samples. Because of this, no quantitative data could be rendered for two of the MRI samples or any of the SSI samples by GC/MS/MS of the jar-extracts. Where quantitative data were obtained for the MRI samples, there was little good correlation between the results using the modified MM-5 train and GC/MS/MS and the unmodified MM-5 train and GC/MS. This is likely due to the variable and non-quantitative properties of the sampling trains toward PCDD/PCDF. Perhaps maintaining the train temperatures higher than 125°C would permit better transmission of PCDD/PCDF to the XAD-2 resin cartridge. Results for PCDD/PCDF analysis by GC/MS and GC/MS/MS of respective XAD-2 resin samples for one of the runs did show a moderately good correlation (see Figure 16) however, this was more the exception than the rule and certainly, with the variability in PCDD/PCDF transmission, the usefulness of such a correlation is questionable.

With respect to the SSI samples, significant amounts of DCDD (and DCDF, T_3CDD and T_3CDF for MRI) were easily detectible by GC/MS/MS, however, we were unable to quantitate these constituents since the response to the isotopically labelled internal standard (^{13}C-TCDD/TCDF) was negligible due to the aforementioned matrix suppression. The DCDD was apparently unaffected by this matrix since it elutes prior to the suppression components. Because the sample matrix is so unpredictable, all quantitation of native compounds must be undertaken by ratioing signals due to native PCDD/PCDF with those of isotopically-labelled internal standards. Quantitation using external standards is highly speculative using either GC/MS/MS or GC/MS. The GC/MS analysis of the cleaned up extracts had no problem quantitating these analytes due to the elimination of the ion source suppressing matrix constituents.

2.3 CONCLUSIONS

1) There are sufficient quantities of PCDD/PCDF in municipal-refuse incinerator stack gas to be detected using the above sampling protocols.

2) The stack sampling apparatus was inadequate for the quantitative (i.e. 100%) transmission of vapour phase PCDD/PCDF to the XAD-2 resin cartridge. Better heat tracing must be used on the stack sampling train to increase transmission to the XAD cartridge.

3) MS/MS analysis demonstrated freedom from interferences from isobaric compounds.

4) As a final QA/QC protocol, a cleaned up sample(s) already run by GC/MS, should be analyzed by GC/MS/MS.

5) Many of the crude XAD-2 resin extracts were sufficiently contaminated with large amounts of organic matter to suppress ion-source chemical ionization capabilities as well as to irreversibly damage several capillary GC columns.

6) More research should be undertaken to mitigate the effects of chemical matrix on GC/MS/MS analysis stressing the development of rapid cleanup procedures.

The results of this phase of the FLY-ASH and STACK GAS research programs are positive enough to represent a significant increase in analytical capability in the area of PCDD/PCDF analysis. The cooperation between the MOE and SCIEX® has contributed substantially to the applications' development of tandem triple quadrupole GC/MS/MS technology, an example of high-technology analytical equipment manufactured in Ontario. This research has benefitted SCIEX® by expanding the application base of its technology as well as providing a more rapid and cheaper method of determining dangerous environmental contaminants such as PCDD/PCDF.

2.4 REFERENCE

1. L. L. Lamparsky, T. J. Nestrick, and R. H. Stehl, Anal. Chem. 51, 1453, 1985.

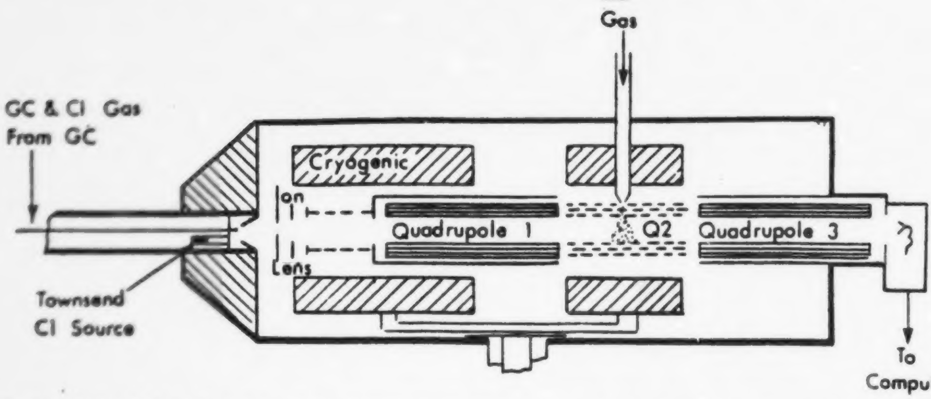


FIGURE 1: SCHEMATIC OF THE TAGA 6000E GC/MS/MS SYSTEM

FIGURE 2: EXTRACTION EFFICIENCIES OF PCDF FROM FLY-ASH: "JAR" vs. SOXHLET METHODS

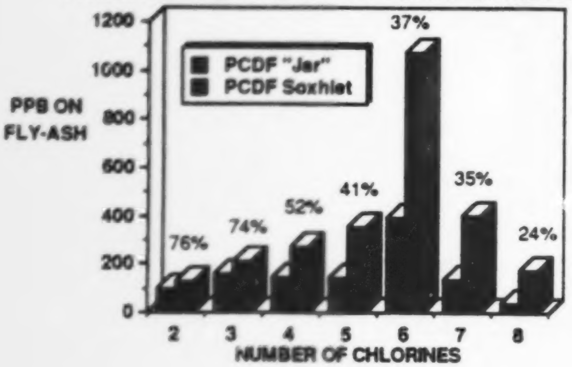


FIGURE 3: EXTRACTION EFFICIENCIES OF PCDD FROM FLY-ASH: "JAR" vs. SOXHLET METHODS

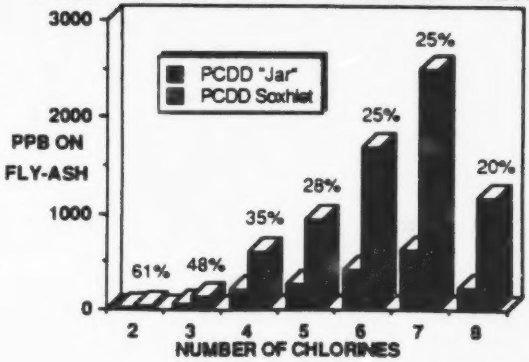


FIGURE 4: PCDF ANALYSIS OF FLY-ASH JAR EXTRACTS BY GC/MS/MS (3 REPLICATES)

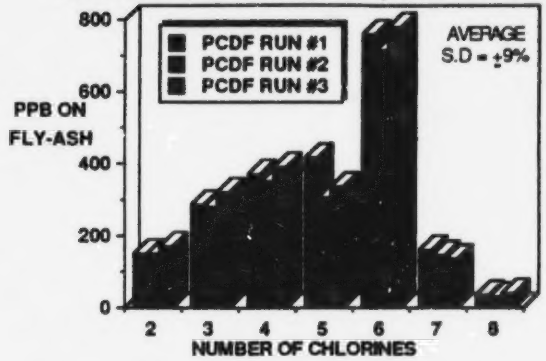


FIGURE 5: PCDD ANALYSIS OF FLY-ASH JAR EXTRACTS BY GC/MS/MS (3 REPLICATES)

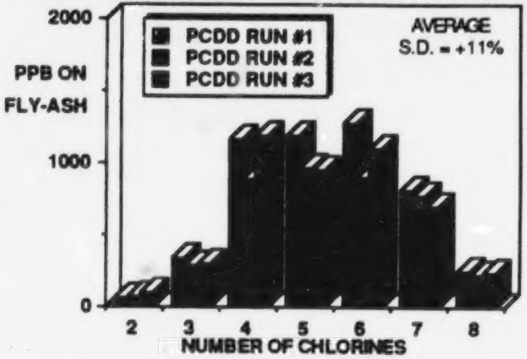


FIGURE 6: PCDD ANALYSIS OF QA/QC FLY-ASH EXTRACTS BY GC/MS/MS AND GC/MS

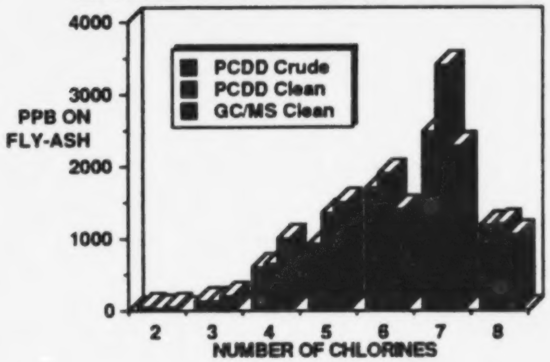


FIGURE 7: PCDF ANALYSIS OF QA/QC FLY-ASH EXTRACTS BY GC/MS/MS AND GC/MS

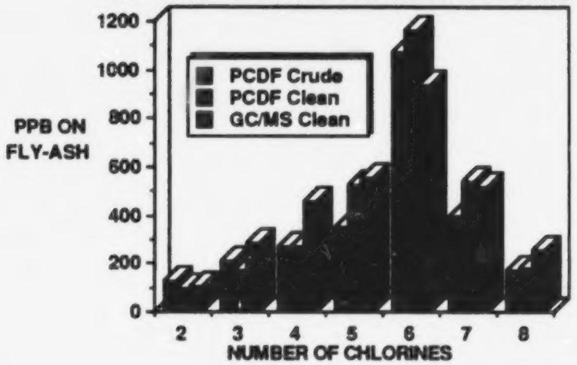


FIGURE 10: COMPARISON OF GC/MS/MS CHROMATOGRAMS FOR TCDD CONGENERS FROM JAR-EXTRACT OF FLY-ASH (TOP) AND STACK-GAS (BOTTOM)

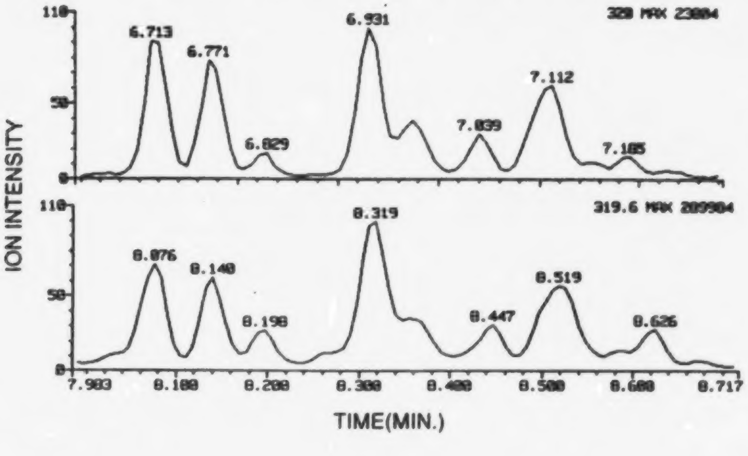


FIGURE 8: MODIFIED MM-5 STACK-GAS SAMPLING CARTRIDGE

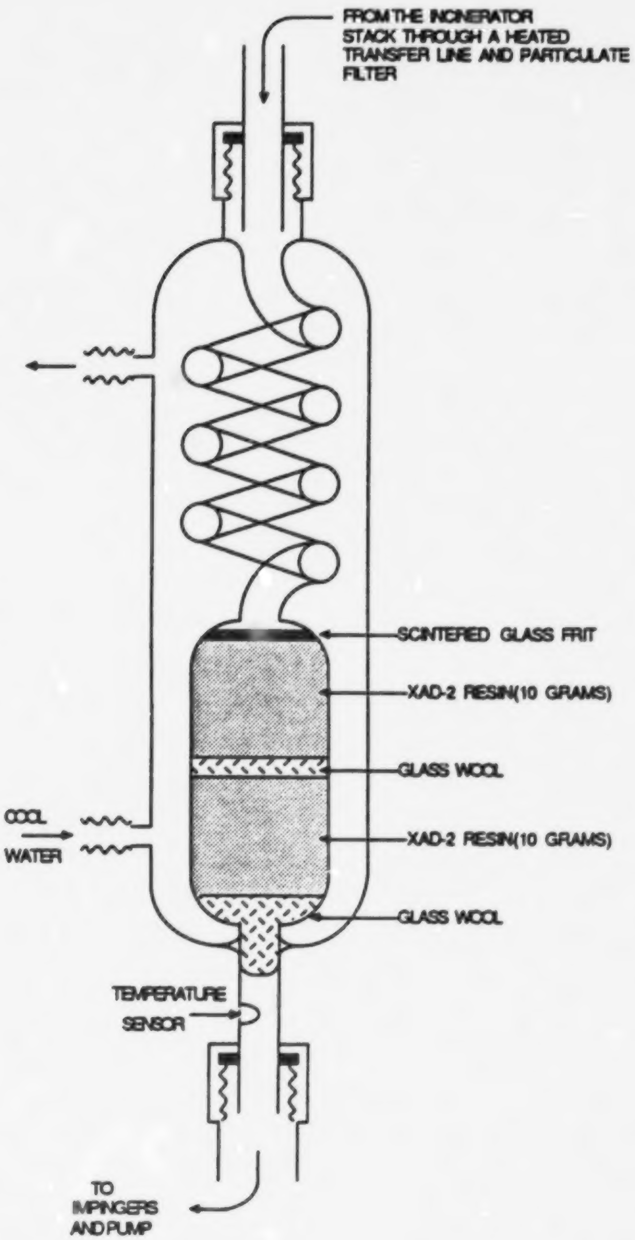


FIGURE 9: SCHEME FOR THE JAR-EXTRACTION OF XAD-2 STACK-GAS SAMPLING TRAP

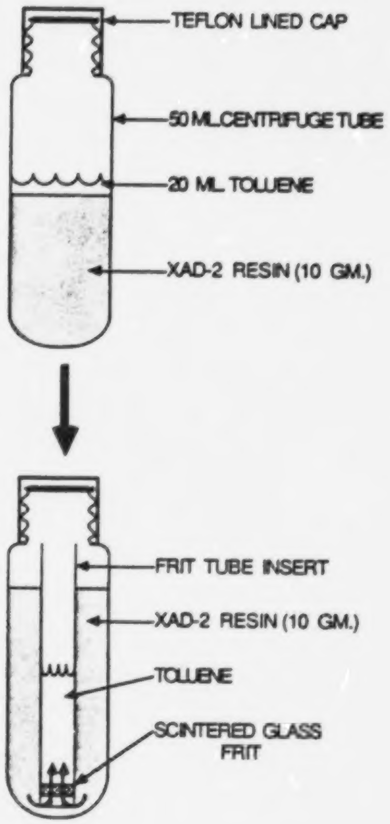


FIGURE11: PCDD & PCDF FOUND IN MUNICIPAL REFUSE INCINERATOR STACK GAS (AVG.4 RUNS)

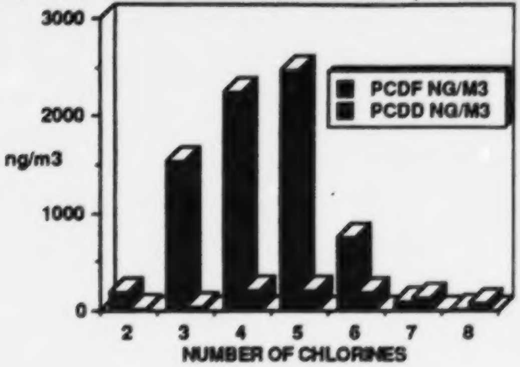


FIGURE 12: PCDD & PCDF IN SEWAGE SLUDGE INCINERATOR STACK GAS (AVERAGE 4 RUNS)

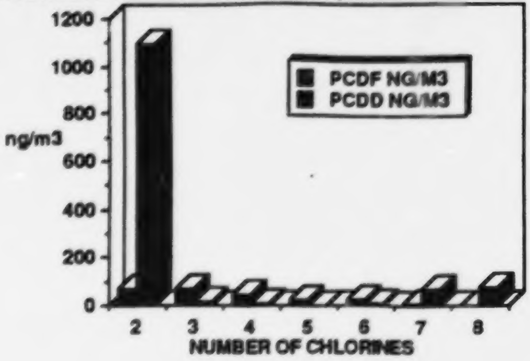


FIGURE 13: PARTITIONING OF PCDF IN MRI TRAIN; PROBE VS. "TRAP" (AVG. 4 RUNS)

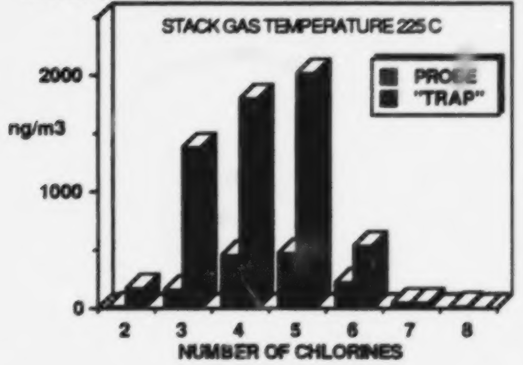


FIGURE 14: PARTITIONING OF PCDD IN MRI TRAIN; PROBE VS. "TRAP" (AVG.4 RUNS)

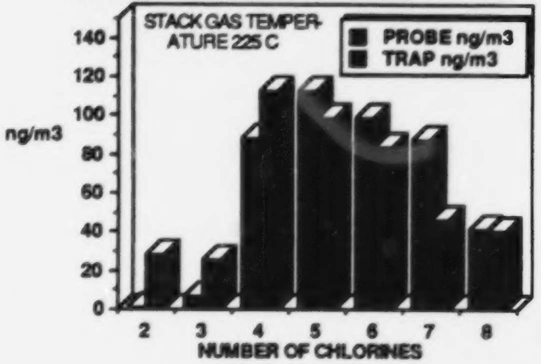


FIGURE 15: PARTITIONING OF PCDF IN MRI TRAIN; RATIO OF PROBE TO "TRAP" (4 RUNS)

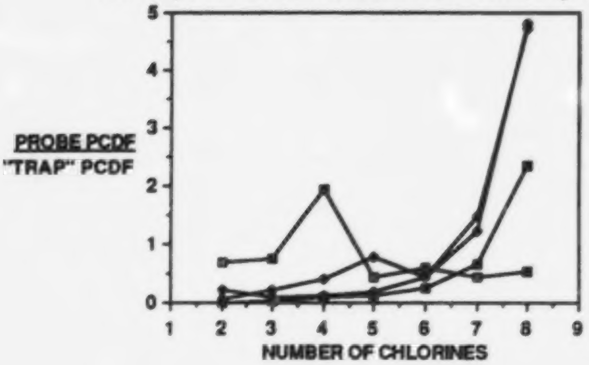
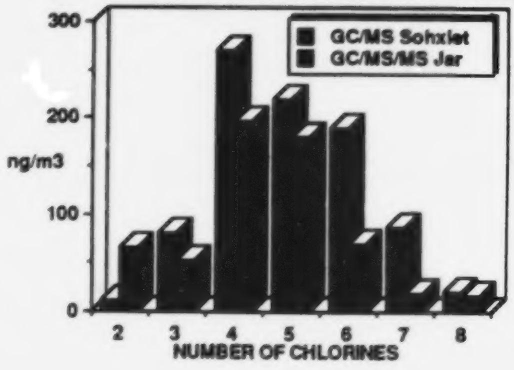


FIGURE 16: PARALLEL TRAIN PCDD LEVELS BY "JAR"-GC/MS/MS VS. SOXHLET-GC/MS



RETROSPECTIVE CORRELATION SPECTROSCOPY AND ITS APPLICATION TO ATMOSPHERIC MONITORING

R. W. Nicholls, M. Amani, M.Mandelman and W.H.Morrow

Centre for Research in Experimental Space Science
York University,
4700 Keele St., North York, Ontario M3J 1P3

INTRODUCTION

Correlation spectroscopy is a powerful tool for the detection, monitoring, and measurement of concentrations of trace atmospheric species. The correlation between the intensity profile of a field spectrum and that of a "mask" which models the spectral "fingerprint" of the molecular trace species in question is a measure of the trace species concentration. The application of the method of correlation spectroscopy to environmental problems is an excellent example of technology transfer from fundamental research to important analytic application fields. The method was first proposed and used by the astronomers Bottema, Plummer, Strong and Zander (1,2) for diagnostic applications of astronomical spectra from balloon-borne payloads. Barringer and colleagues (3,4) developed the method for environmental applications.

Two types of correlation spectrometer have been developed: dispersive and non-dispersive, and early versions of both types of instrument were analogue in nature. Dispersive correlation spectroscopy as originally proposed, and as developed into the COSPEC instrument by Barringer Research Ltd, involves phase-sensitive detection of the total signal from that part of a field spectrum which passes through a focal-plane mask (of alternate transparent and opaque regions which is an analogue representation of the absorption spectrum of the species of interest) regularly oscillated in the direction of the dispersion.

In the nondispersive instrument, which is a modern deriviatve of R.W.Wood's (5) early experiments in resonance radiation, extended by Luft (6) and Goody (7), the analogue mask and the effective dispersion is achieved by using a chopper gas cell containing the vapour of the trace species to be sensed remotely. Ward and Zwick (8), then at Barringer Research Ltd., developed a field nondispersive instrument called GASPEC, the principle of which is, from their paper:

" The main feature is a pair of gas cells. The sample cell contains a judiciously chosen quantity of target gas to be sensed while the reference gas cell contains a spectrally inactive gas. The optical depth of the target gas in the sample cell is optimised for a maximum production of the modulation of the target gas energy and average transmission. Inmcoming radiation characteristic of the target is selectively filtered by being absorbed in the sample cell, but is readily transmitted through the reference cell. Therefore the radiance transmitted through the sample cell is largely independent of the presence of target gas signature in the received spectrum whereas the radiance transmited through the reference cell is strongly dependent upon the presence of the target gas. The difference between the spectral transmittance of the two cells is thus a sensitive indicator of the amount of target gas signature in the radiation received by the sensor."

GASPEC was a derivative of the Barringer bread board model of a satellite borne non-dispersive gas filter remote sensor used by Riechle (9) of NASA as part of the MAPS (Measurement of Air Pollution from Satellites) instrument flown as part of the OSTA satellite payloads on Shuttles STS-2 (1981) and STS-41G (1984) for global measurements of the atmospheric mixing ratio of carbon dioxide in the middle and upper troposphere. This is part of the new thrust in international earth and atmospheric studies in which a global view is taken of most aspects of the earth as a system.

GASPEC and the NASA instrument were analogue instruments based on the technologies of the mid-1970's, and extreme engineering care had to be taken to compensate for drifts in the analogue signal.

In this paper a brief discussion is made of our recent work to place both of the correlation spectroscopy methods on a digital basis.

2: RETROSPECTIVE DISPERSIVE CORRELATION SPECTROSCOPY

2.1: Principle of the Method

One of the limitations of the analogue method is that it calls for the use of a specific analogue mask to be installed in the spectrometer for each "target" species. Thus searches for more than one species at a time are not easily carried out. To overcome this, the basic concept of the retrospective method was proposed (11), (12). In this method, the field spectrum (of for example a smoke plume against skylight (10)) is recorded digitally and stored on diskette or tape, for later retrospective interrogation by any suitable digital mask functions, each one of which is representative of the absorption spectrum of a trace species of interest. The numerical mask can either represent the true absorption cross section spectrum of the species in question, or can represent a series of alternating transparent and opaque regions (similar to analoge correlation mask).

If I(L) is the incident radiance of the field spectrum where I is intensity and L is wavelength, and M(L-Z) is the mask function displaced in register by Z, then the correlogram between the mask function and the field spectrum is:

$$C(z) = \int I(L)\ M(L-Z)\ dL \qquad (1).$$

Under optically thin conditions:

$$I(L) = I_o(L) \exp\left[-N\ X\ \sigma(L)\right] = I_o(L)\left[1 - N\ X\ \sigma(L)\right] \qquad (2)$$

where X is the path length of absorber, N is its number density and $\sigma(L)$ is the absorption cross section. In short wavelength increments in the visible region of the spectrum $I_o(L)$ does not very very rapidly and may sometimes be treated as a constant. Thus (1) is

$$C(Z)/I_o = A - NX\ F(Z) \qquad (3)$$

$$\text{where } A = \int M(L-Z)\ dL = \text{Total mask area} \qquad (4)$$

$$\text{and} \quad F(Z) = \int \sigma(L)\ M(L-Z)\ dL \qquad (5)$$

which is the convolution between the optical cross section and the mask function. Equation (3) provides a new direct method for determination of the column density NX of absorber. A plot of $C(Z)/I_o$ vs F(Z) has an intercept of A and a slope of NX. For many absorbers of interest $\sigma(L)$ is known from the literature, and I_o is in principle known from field circumstances. It is this possible retrospectively to calculate C(Z) and F(Z) from digital measurements and thereby to determine NX. In cases where $I_o(L)$ is not constant, eg in the UV near 3000A, it is known (10) and can be is included in each of the integrals of equations (4) and (5). During the second year of the grant, equation (3) was modelled analytically using simple reasonable functional forms for $\sigma(L)$ and M(L-Z), and a function form for C(Z) determed in terms of error functions. This work has been reported previously (11) (12). During the past year the diagnostic implications of the method have been more rigorously investigated as reported below for a real molecular case and compared with laboratory measaurements.

The practical diagnostic utitlity of equation (3) has been confirmed.

2.2: Analytic and Digital Studies

The earlier idealised model studies (12) have been greatly extended by Mr. Amani. They have treated a) three types of case of non constancy of $I_o(L)$ (Linear, Exponential and Planckian variation with wavelength), b) more realistic models of o (L) particularly for SO_2 than the equally spaced gaussian comb used in the earlier work, and c) a wide variety of mask functions. These analyses are be reviewed in detail in the oral presentation of this work. When there is a strong L-dependence of I_o, equation (3) becomes somewhat more complex, and C(Z) is linear with respect to a sum of functions including the convolution of σ and M, and others which arise from the functional form of $I_o(L)$. In principle this case is no more difficult to use than the more idealised equation (3). The actual cross section of SO_2 taken from the literature, and from our laboratory measurements was modelled analytically in this work. It was found that the greater the separation of spectral features (the greater the resolution) the better the method works. Ideally the interfeature separations should be greater than the feature widths.

2.3 Test of the diagnostic method against laboratory measurements.

Dr. Mandelman set up one of our digital scanning spectrometers in the laboratory. It was equipped with a Hamamatsu UV photomultiplier. A deuterium continuum lamp was used to provide I_o, and an SO_2 cell placed in the parallel pre-slit beam. A suitable vacuum system for SO_2 handling was set up which allows for fractional distillation of solid/liquid SO_2 to remove high boiling point impurities.
Using this equipment Dr. Mandelman provided a digital database of I(L) vs L for a number of SO_2 concentration levels. Using the digitised spectra and digitised σ(L) values for SO_2, an extensive study of the diagnostic application of equation (3) was made by Mr.Amani. Much work went into mask optimisation. The predicted straight line plots were obtained whose slopes were consistent with the experimental values of NX to a few percent. This confirmation was very encouraging. More work is needed to develop the method further for routine field applications. This should be straightforward. Similar work needs to be done for the case of other species of interest (eg NO_2 whose σ(L) does not have many well separated feastures.

3: GAS FILTER NON-DISPERSIVE CORRELATION STUDIES

Two non- dispersive gas filter digital correlation instruments, GASCOFIL (which is small, hand held and non-scanning) and GASCOSCAN (which is a larger spectral scanning instrument) have been developed by Mr. Morrow as passive, owd folded path active remote sensors of trace atmospheric constituents with the support of NSERC strategic grants. Depending on sensor/ filter combinations they operate from the 3000A UV cut off to 9 microns. Each is completely computer operated. Small microprocessor circuits act as controllers of the rotation of the gas call filter wheels, as controllers of the spectral scan, as controllers of the data collection, storage, real-time display and analyses. In the oral paper these instruments will be described, and measurements taken in field situations will be presented and discussed.

REFERENCES

(1) M. Bottema, W.Plummer and J.Strong: Astrophysical Journal, 139, 1021, 1964
(2) M.Bottema, W.Plummer, J. Strong and R.Zander: Astrophysical Journal, 140, 1640 (1964)
(3) A.R.Barringer: "Remote Sensing of Vapours as an Airborne Remote Sensing Tool" Proc. Int. Symp. on Remote Sensing (1964) pp 279-292, Univ. Mich. Press Ann Arbor 1965
(4) A.R.Barringer and J.R.Shock: "Progress in the Remote Sensing of Vapous for Air Pollution, Geologic and Oceanographic Applications" Proc. 4th Int. Symp. Remote Sensing (1966) Univ. Mich Press Ann Arbor
(5) R.W.Wood: "Physical Optics, 3rd Edn, McGraw Hill,1934
(6) K.R.Luft: Jounral of Technical Physics 24, 97, 1943
(7) R. Goody: Journal of the Optical Society of America 58 900 1960
(8) T.V.Ward and H.H.Zwick: Applied Optics 14, 2879 1975
(9) H. Reichle "Results of a Tropospheric CO Measurement experiment flown in the Space Shuttle" pp WC3-1 to WC3-4, Technical Digest of Optical Society of America Topical Meeting on Optical Remote Sensing of the Atmopshere, Jan 1985.
(10) M. Iqbal: "An Introduction to Solar Radiation", Academic Press NY,1983
(11) R.W.Nicholls: Procedings of the 1984 OME Technology Transfer Conference pp 945-969
(12) R.W.Nicholls: Applied Optics 24, 2046-2048,1985

MEASUREMENT OF ATMOSPHERIC GASES BY TUNABLE DIODE LASER ABSORPTION SPECTROMETRY

H.I. Schiff, G.W. Harris and G.I. Mackay
Unisearch Associates Inc.
222 Snidercroft, Concord, Ont. Canada.

Summary

The advantages of Tunable Diode Laser Absorption Spectrometry (TDLAS) for measuring trace atmospheric gases are universality, positive identification, good sensitivity and rapid response time. An instrument has been constructed which can measure two gases simultaneously under automatic computer control with detection limits better than 100 parts per trillion and with response times better than 5 minutes. Procedures have been established for the measurement of NO, NO_2, HNO_3, NH_3, H_2O_2 and HCHO. These species have been measured under a variety of conditions in smog chambers and in ambient air from mobile laboratories and from aircraft.

1. INTRODUCTION

Tunable diode laser absorption spectrometry offers an attractive method for atmospheric measurements (1). Almost all gases of atmospheric interest absorbs in the 2 to 15 micron region. The very high spectral resolution of tunable diodes permit selection of a single rotational-vibrational line which makes interferences from other gases very unlikely. If an accidental interference should happen to occur it can readily be identified by a change in line shape and another line can be chosen. Unequivocal proof of the absence of interference is obtained by measuring the concentrations at 2 different lines. The probability of identical interferences at 2 different lines is vanishingly small (2).

To get the desired sensitivity and detection limit a long absorption path can be obtained by using a multi-pass White cell. The absorption line can be scanned in a fraction of a second and the response time of the measurement is normally limited by the residence time of the sampled gas in the White cell which is typically a few seconds.

2. DESCRIPTION OF THE INSTRUMENT

Figure 1 shows the schematic of a TDLAS system designed to operate in field conditions from a mobile laboratory. Each of the two cryostats has a laser source assembly containing 4 laser diodes. One laser diode from each assembly can be selected to permit a choice of two gases to be measured simultaneously. The emitted radiation from each of the selected diodes is scanned over the selected line by changing the current through the laser.

The laser beam from each head is focussed by a lens and then directed to a selection mirror, S which flips back and forth to permit the beam from each of the diodes to enter the White cell in turn.

The 45° angle of the entrance window to the White cell splits the laser beam. Most of the beam passes through the window into the White cell but about 5% is reflected through a cell containing high concentrations of the target gases onto a separate HgCdTe detector. The output from this detector is used to lock the laser radiation wavelength to the center of the absorption line.

The beam enters the 0.84 meter White cell, lined with Teflon, and undergoes 40 passes before exiting to the detector. Absorptions as low as 10^{-5} can be measured. With a total path length of 40 m this corresponds to detection limits in the range 0.1 to 0.3 parts per billion (1 ppbv = 10^{-9}) for most atmospheric gases.

Sampled air enters through an inlet, flows down the tube and is exhausted at the other end. A restriction at the inlet end and a servo valve at the exhaust end maintains the flow rate and the pressure in the cell constant. Keeping the cell pressure at 25 Torr reduces pressure broadening of the absorption line to increase the sensitivity and to minimize the possibility of interferences from other gases.

The spectrometer is operated in the frequency modulated (2f) mode which results in an increased signal-to-noise ratio compared to using direct absorption.

The unit operates under computer control. Laser temperature and current selections for each species are input to the computer. The system is then switched to automatic mode and can operate unattended for at least 24 hours.

The computer signals the selection mirror to position itself so that one of the beams enters the White cell. A ramp voltage is then produced with 128 steps over a range just wide enough to encompass the absorption feature used for the measurement of species A. The line is scanned under computer control at a rate of approximately 10 Hz for 3 seconds (the approximate residence time of the gas in the White cell) and an accumulated "2f" line shape is acquired.

At the end of the 3 sec averaging period the signal on the reference channel, D2 is checked. If the reference channel indicates that the line is not exactly at the center of the 128 step ramp the computer adjusts the laser temperature to bring the line back to the center.

The selection mirror is then commanded to bring the second beam into the White cell and the measurement procedure is repeated for species B. Each species is thus measured once every 6 sec. Data is accumulated in this way for a period of, for example, 3 min providing an average value for the "2f" line shapes over that time frame. The data set, which provides one mixing ratio for each species, is then stored on the computer disk.

The computer manipulates the solenoid valves and flow controllers to perform measurement and calibrations sequences automatically. In a typical sequence the valve system is commanded to flow either zero or scrubbed, ambient air through the White cell. Background spectra of the components are obtained by scanning over the wavelength regions of the selected absorption lines. A typical example is shown in Figure 2a.

Calibration gas is then added to the zero (or scrubbed) air flow and allowed to stabilize for approximately 1 min. An averaged calibration spectrum is then obtained for 3 min which also serves as a reference spectrum and the raw data is archived (Figure 2b).

The background spectrum is subtracted (channel by channel) from the reference spectrum. This procedure removes any frequency dependent structure in the background and reference spectra which remains stable for the averaging period . The result of this subtraction is shown in Figure 2c.

Valves are then reset to admit ambient air, and after another stabilization period an ambient air spectrum is acquired for 3 min (Figure 2d) and the background spectrum subtracted (Figure 2e). The net ambient spectra is least square fitted to the net reference spectrum. The same calibration sequence is followed for both gases being measured.

The frequency of calibration and the time duration of the various stages of the sequences can be altered by the operator. The choice depends on the mixing ratios of the species being measured; low ambient concentrations require more frequent determination of background and reference spectra.

3. MEASUREMENT REQUIREMENTS

The use of the system to measure an atmospheric component has 3 requirements: (1) selection of a laser and an absorption feature; (2) establishment of a calibration procedure; (3) ensurance of sampling integrity.

The selection of a laser and an absorption feature represents a compromise between the absorption line strength, the characteristics of the laser emission at the wavelength of the line, and absence of interferences at this wavelength from other atmospheric gases.

The calibration philosophy calls for the addition of a known amount of the calibration gas to the sampled air stream at the entrance to the sampling line. The concentration of the "spike" is chosen to provide an increase in measured mixing ratio comparable to the mixing ratio of the gas in the ambient air. In this way, any surface effects that may occur will be the same for the sampled and spiked air and should therefore be compensated.

Finally, tests are performed to ensure sampling integrity. The air sample is continuously drawn through a short length of 6 mm teflon tubing and the pressure reduced by an all Teflon needle valve. The flow rate of the sampled air is typically 6 SLM giving a residence time of a tenth of a sec in the sampling line and 3 sec in the White cell. The response time of the system is defined as the time required for the signal from an addition of the species to drop to 90% of its value when the source is removed or the time for the signal to reach 90% of its final value when the source is introduced. Response times greater than the residence times are indicative of interaction of the gases with the surfaces of the sampling system and has been observed for HNO_3, NH_3 and H_2O_2. In those cases careful studies were performed to assess the nature of the surface processes and sufficient sampling time is allowed for the system to reach steady state with the ambient air.

These procedures have been established for NO, NO_2, HNO_3, NH_3, SO_2, HCHO, and H_2O_2 and measurements of these gases have been made under field conditions and in smog chamber experiments.

4. EXAMPLES OF ATMOSPHERIC MEASUREMENTS

Bottled gas of NO in N_2 at a concentration of a few ppmv, traceable to a National Bureau of Standards determination, has been used as the calibration source for NO. The response time of the system for this gas is the residence time in the cell of 3 sec. The minimum detection limit, MDC, is defined as a signal to noise of one, is better than 100 pptv (1 pptv = 10^{-12}).

A commercial permeation tube is used for the calibration source for NO_2. The permeation rate is determined by weight loss and also checked by NO/O_3 titration with NO then serving as the calibration standard. The response time and MDC are 3 sec and 100 pptv.

Figure 3 shows typical diurnal variations of NO_2 concentrations measured at a relatively clean rural site. Peak concentrations of about 3 ppbv decrease during the day as photochemistry proceeds and increases again after sunset, (~ 8 p.m). Oxidation by O_3 decreases the NO_2 concentration during the night.

Figure 4 shows an example of the higher concentrations observed in a relatively polluted urban environment. Diurnal variations are similar with mixing ratios as high as 150 ppbv observed. This figure also shows an interesting example of how the TDLAS technique can be used to serve as a reference method against which other, less definitive methods can be compared. Simultaneous measurements were also made with a LUMINOx instrument based on chemiluminescence from a luminol solution. The two methods agree except for two nights when the pollution levels were quite high. On these occasions the luminol method gave values some 35% higher than the TDLAS method, indicating that the luminol method was also responding to some other species present under these conditions at night.

The line strengths for HNO_3 are about 4 times lower than for NO_2 resulting in an MDC of about 300 pptv. The calibration source for HNO_3 is a specially designed permeation device in which the carrier gas is passed through a Teflon tube immersed in a solution of HNO_3 and H_2SO_4 acids. The permeation rate is determined by potentiometric titration with standard NaOH solution. Sampling integrity is the major problem with measuring HNO_3 since this gas is highly polar and absorbs readily on most surfaces. The response time of the system decreases with increasing flow rate of the sampled air through the system and is about 5 min for flow rates greater than 6 standard liters per minute (SLM).

Figure 5 shows typical diurnal behavior of measurements of HNO_3 taken at a rural site. The concentration peaks in the early afternoon and decreases rapidly in the late afternoon and evening, indicative of the rapid dry deposition rate of this species. The rapid dry deposition is also demonstrated in Figure 6 which shows difference between measurements made at heights of 1 m and 8 m above a snow surface.

The line strengths for NH_3 are high permitting detection limits of 100 pptv. But, like HNO_3, NH_3 is a "sticky" molecule requiring air flows through the system of at least 6 SLM to provide response times of 5 min. The calibration source is a gas cylinder containing NH_3 in N_2 having a concentration of a few ppmv which is checked periodically by potentiometric titration with standard acid.

Figure 7 shows simultaneous measurements made of NH_3 and HNO_3 at a rural site. The measurements show indication of anticorrelation which suggests mutual neutralization. However the product of the concentrations is much less than the equilibrium values with solid NH_4NO_3 and it is more likely that the anticorrelation results from mixing of different air masses.

For calibration of H_2O_2 carrier gas is flowed through a 4 m coil of polyethylene immersed in a 50% solution of stabilized H_2O_2. The permeation rate of this device was determined by a modification of the colorimetric $TiCl_4$ method. The response time for H_2O_2 is about 40 sec; apparently some conditioning time with the apparatus is required for this species but much less than is required for HNO_3 or NH_3.

The relatively weak line strengths for hydrogen peroxide limits the detection of hydrogen peroxide to between 300 and 600 pptv for 5 min integration times with the system described above. Measurements made with this system showed that the H_2O_2 mixing ratios in ambient air is generally less than this detection limit. Modifications were therefore made in the system which consisted of increasing the base path of the White cell to 1.5 m and using improved, astigmatic entrance and exit optics. These modifications permitted a total path length of 200 m to be achieved with a concommitant improvement in detection limit. With the new system detection limits for H_2O_2 of at least 100 pptv were obtained. The improved system gives detection limits for NO_2 and HNO_3 of 25 and 75 pptv respectively.

Figure 8 shows an example of H_2O_2 measurements made under relatively polluted conditions and Figure 9 shows measurements made under relatively clean conditions. Both studies showed similar diurnal variations with concentrations reaching maxima in the afternoon and minima during the night. The mixing ratios reach higher values in the clean air conditions.

The calibration source for formaldehyde is a Teflon permeation device containing paraformaldehyde. The permeation rate is determined by a modification of the chromotropic acid colorimetric method. No sampling problems are encountered with this gas and the response time of the system is the 3 sec residence time. The detection limit for HCHO with the improved system is better than 50 pptv.

Figures 10 and 11 show examples of H_2CO measurements under the same conditions as shown for H_2O_2 in the preceding figures. For the polluted site the peak concentrations were observed near local noon. For the relatively clean site the peak occurred somewhat later in the afternoon and was considerably lower than for the polluted site.

The TDLAS system has also been used to measure these gases in smog chambers. A modified version of the system in which a liquid N_2 Dewar was substituted for the helium cryostat was flown successfully in and above the boundary layer over the eastern Pacific to measure NO_2 and HNO_3.

5. CONCLUSIONS

The tunable diode laser absorption spectrometer has been shown to be a very versatile system for measuring trace atmospheric gases from mobile laboratories and from aircraft under a number of ambient and smog chamber air conditions. Its high specificity, good sensitivity and rapid response time makes it a very suitable standard against which other less definitive methods can be compared.

REFERENCES

(1) Schiff,H.I., Hastie D.R., Mackay G.I., Iguchi T and Ridley B.A. (1983) Tunable diode laser systems for measuring trace gases in tropospheric air. Envir. Sci. Technol. 17, 352A - 364A.

(2) Slemr F., Harris G.W., Hastie D.R., Mackay G.I. and Schiff H.I., (1986) Measurement of gas phase hydrogen peroxide in air by tunable diode laser absorption spectroscopy. J.Geophys. Res. 91, 5371-5378.

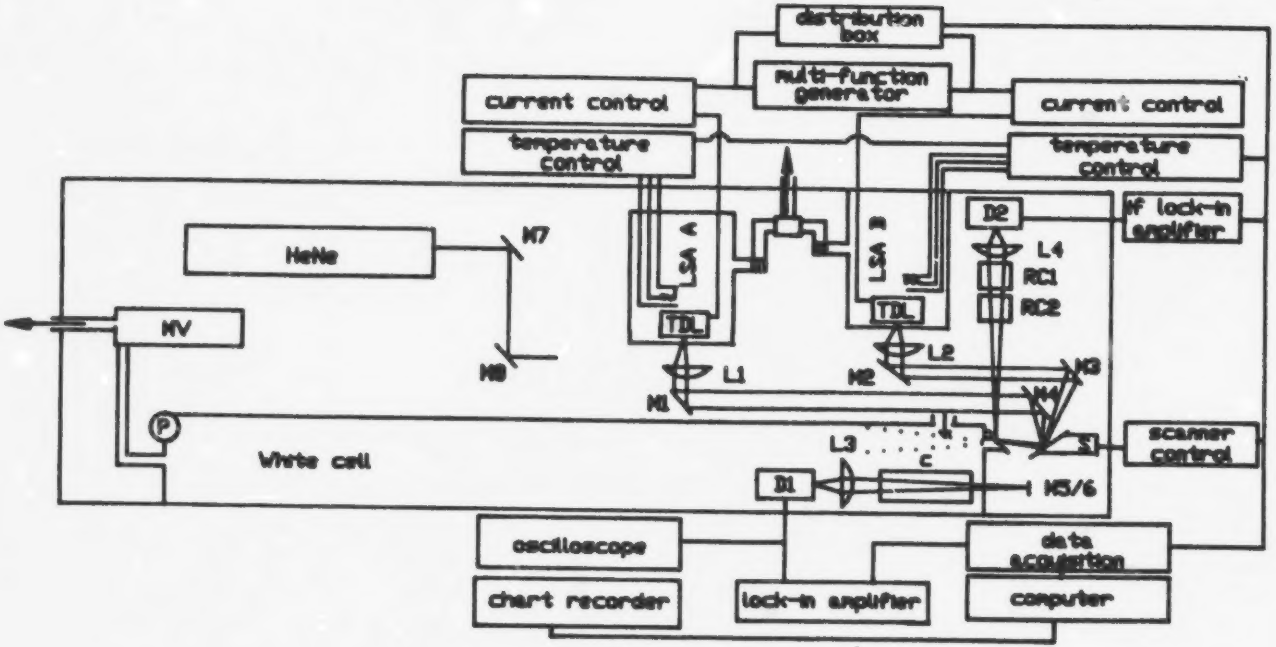
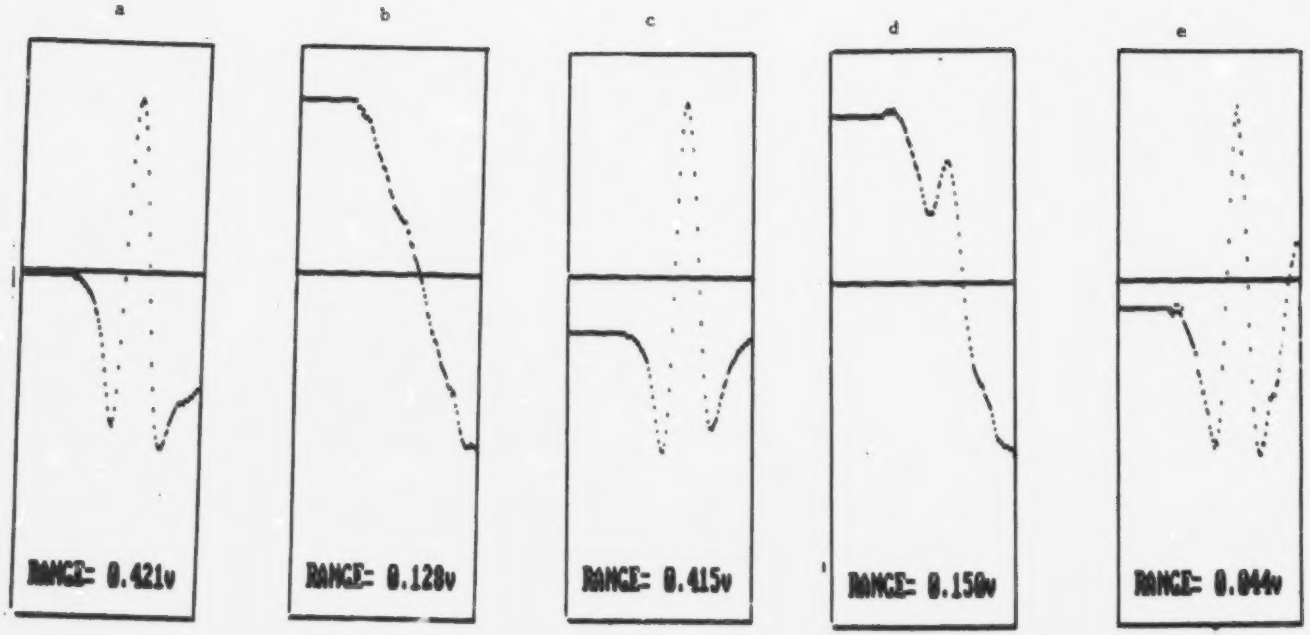


Fig 1: Schematic of the optical system and control electronics



```
mean mixing ratio =  0.133+/- 0.007 ppb
correlation coeff. = 0.978
```

Fig 2: Computer screen printouts for NO_2 aircraft measurements.

(a) raw calibration spectrum; (b) raw background spectrum; (c) calibration spectrum, background subtracted; (d) raw ambient spectrum; (e) ambient spectrum, background subtracted.

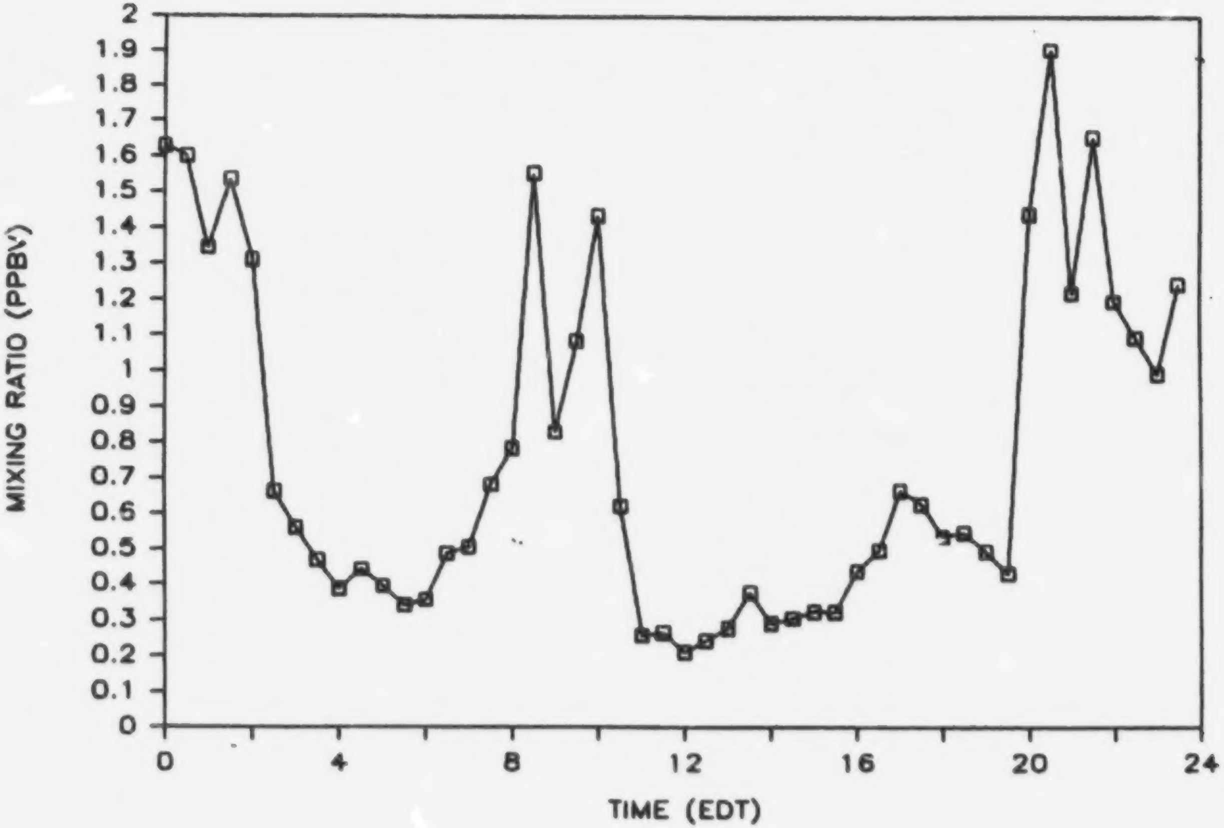


Fig 3: 30 min average NO_2 measurements made at Cold Creek, Ontario on June 25, 1985

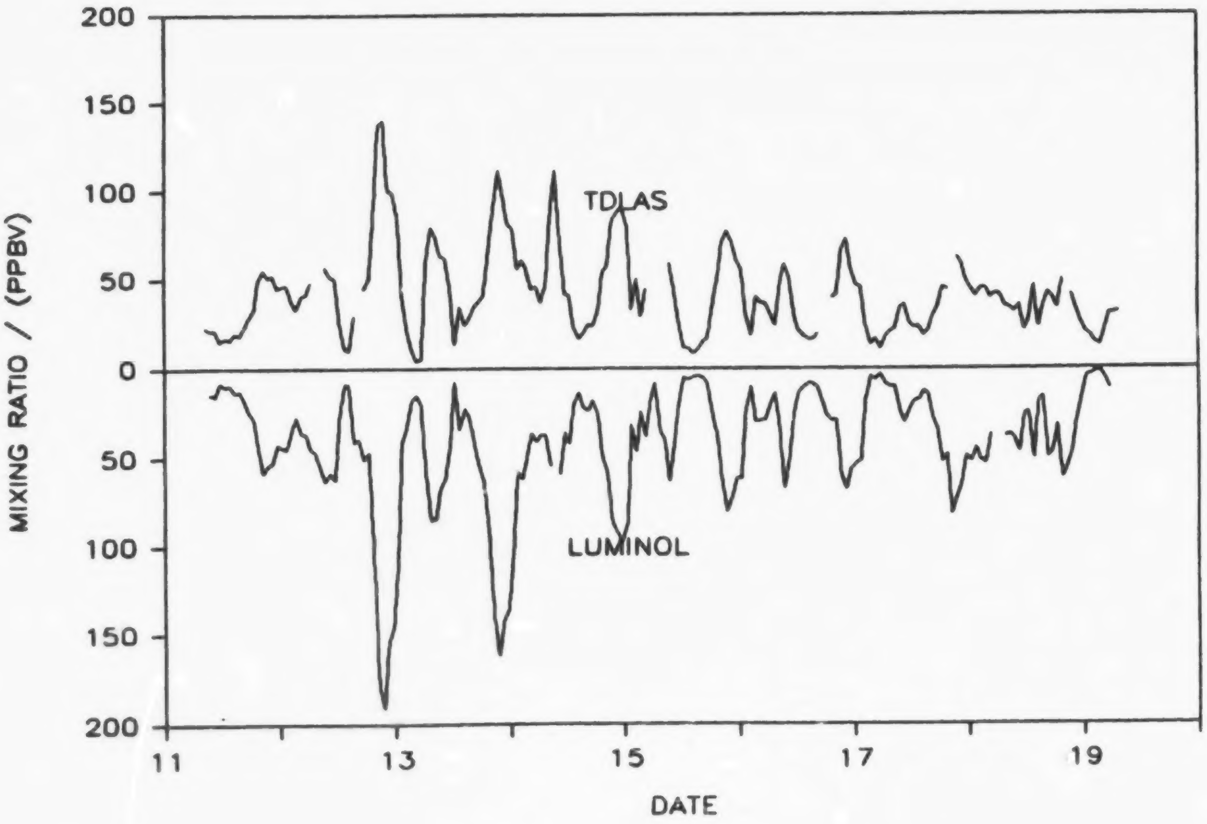


Fig 4: Comparison between 1 hr NO_2 measurements made simultaneously by the TDLAS and the LUMINOX instruments at Claremont CA during September 1985.

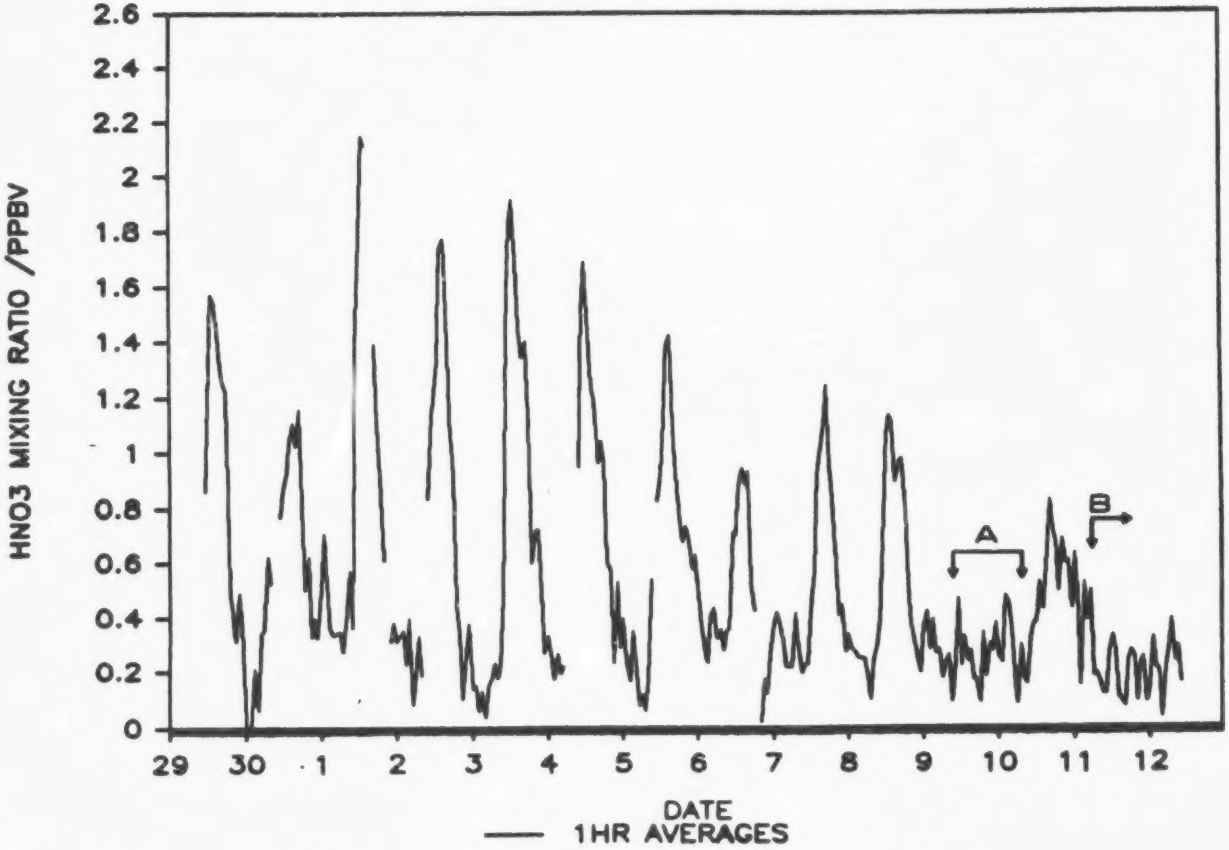


Fig 5: hourly average HNO_3 measurements at Rayleigh NC Sept 29 - Oct 12. annular denuder in front of inlet during period A, heavy rain during period B.

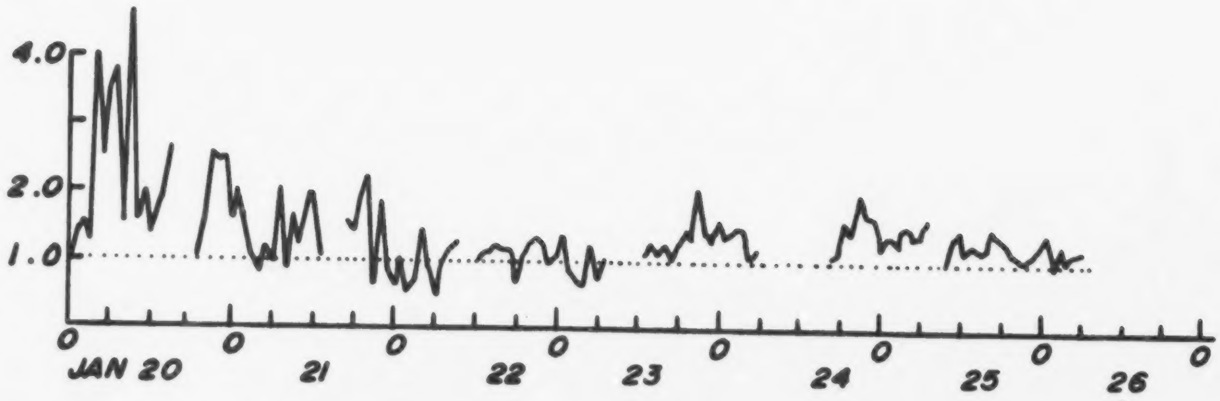


Fig 6: Average ratios of HNO_3 mixing ratios measured at 8 M and 1 M above a snow surface at State College, PA from Jan 20-26, 1984.

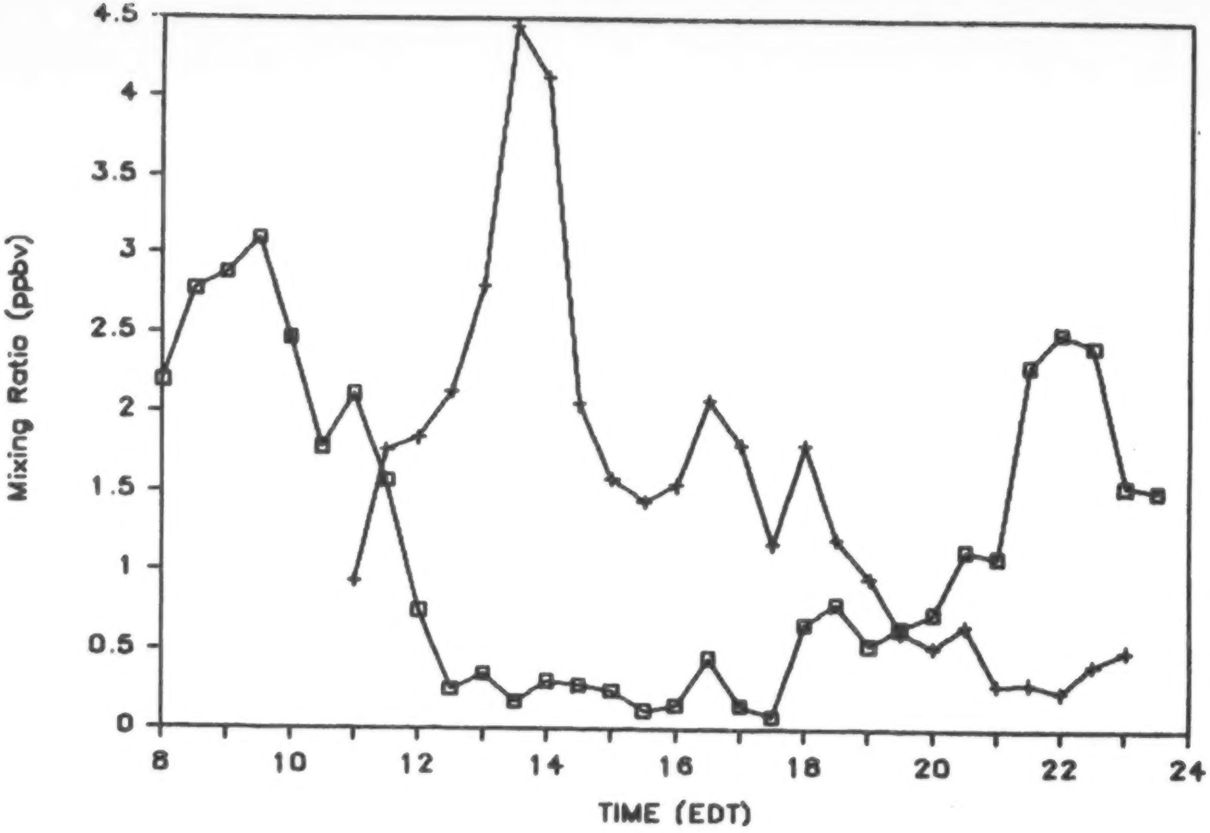


Figure 7: 30 min average mixing ratios measured at Cold Creek, Ont. July 5, 1985
+ NH_3 HNO_3

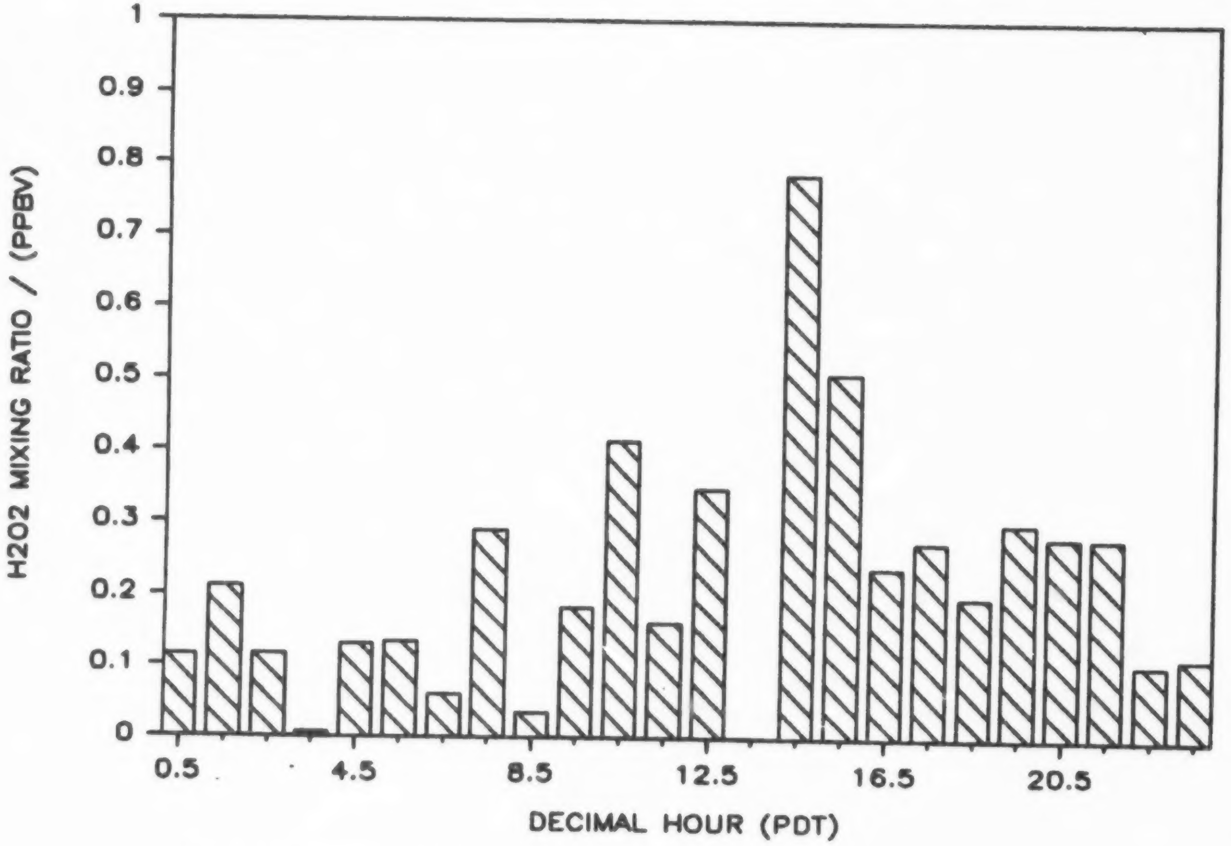


Fig 8: hourly averaged H_2O_2 mixing ratios at Glendora CA on Aug 12, 1986.

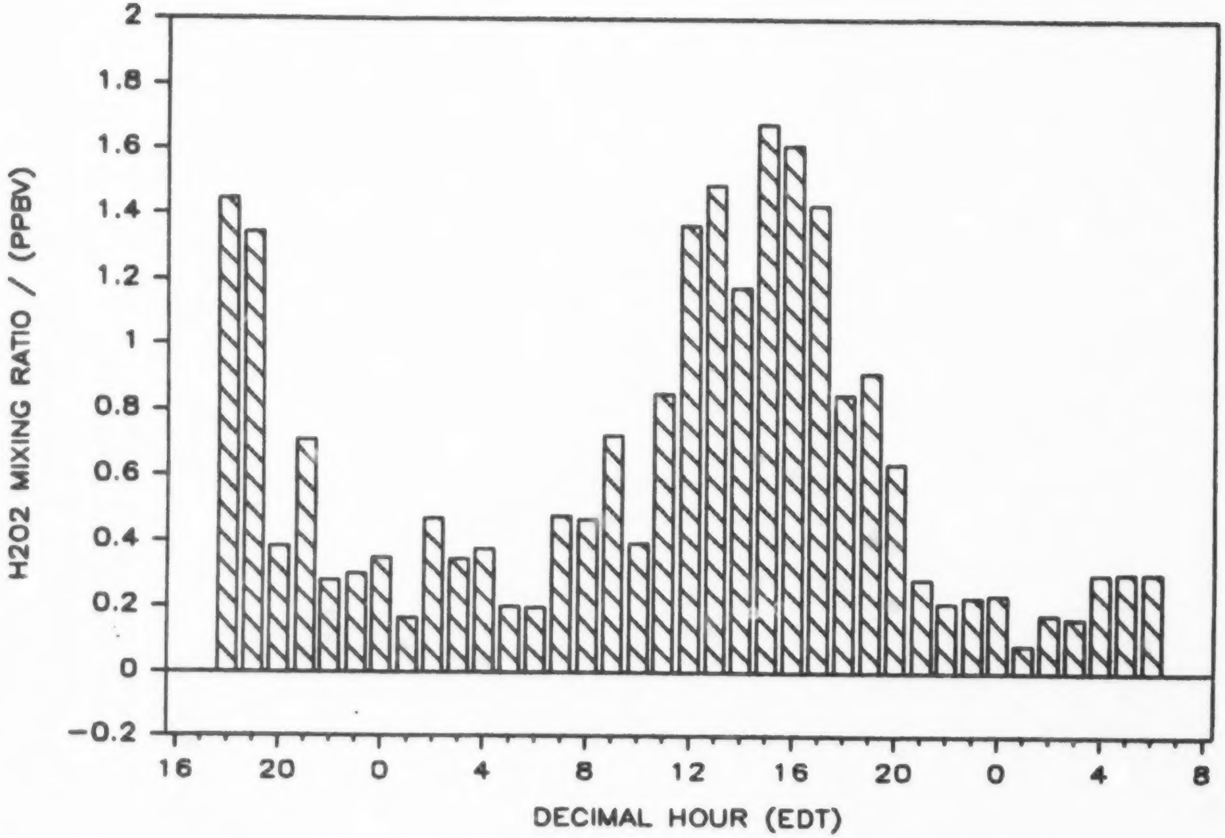


Fig 9: hourly averaged H_2O_2 mixing ratios of H_2O_2 at Rayleigh NC between June 24 and June 26, 1986

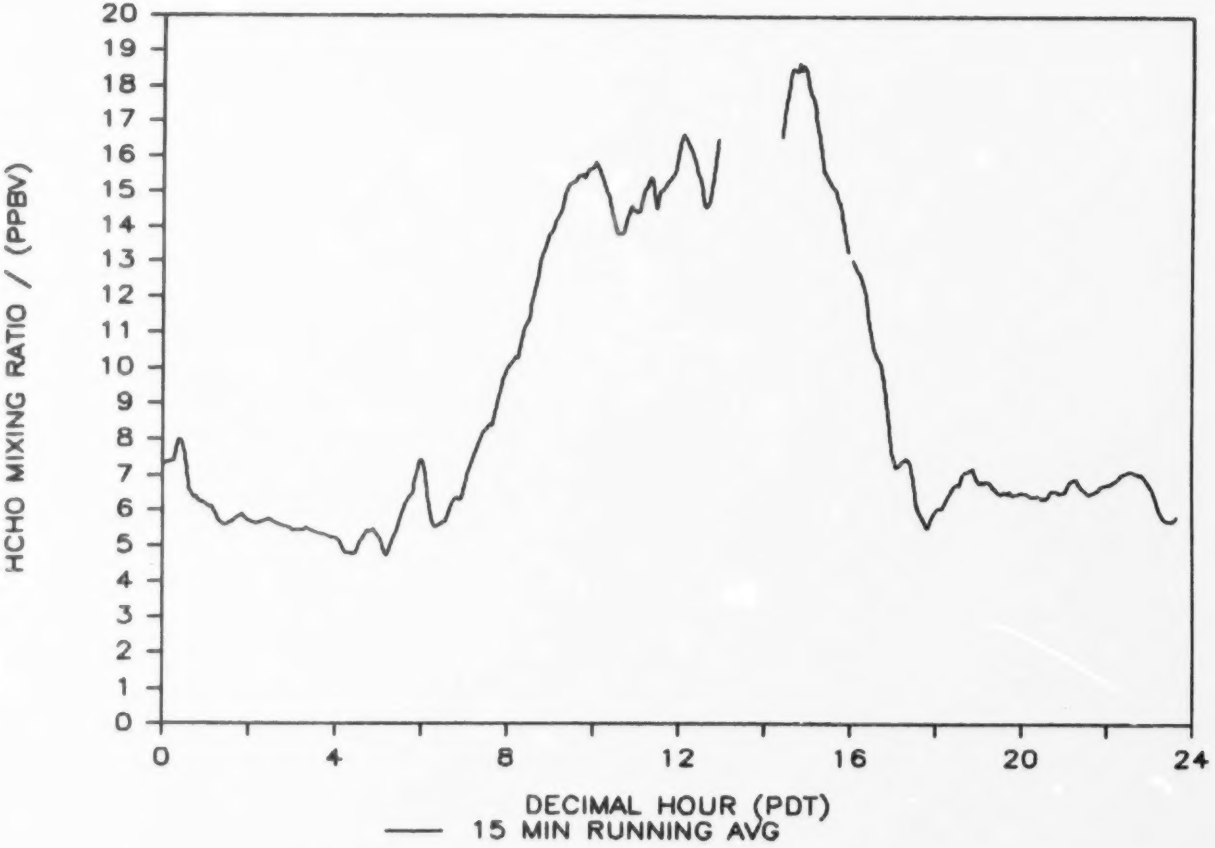


Fig 10: HCHO mixing ratios at Glendora CA on Aug. 12, 1986.

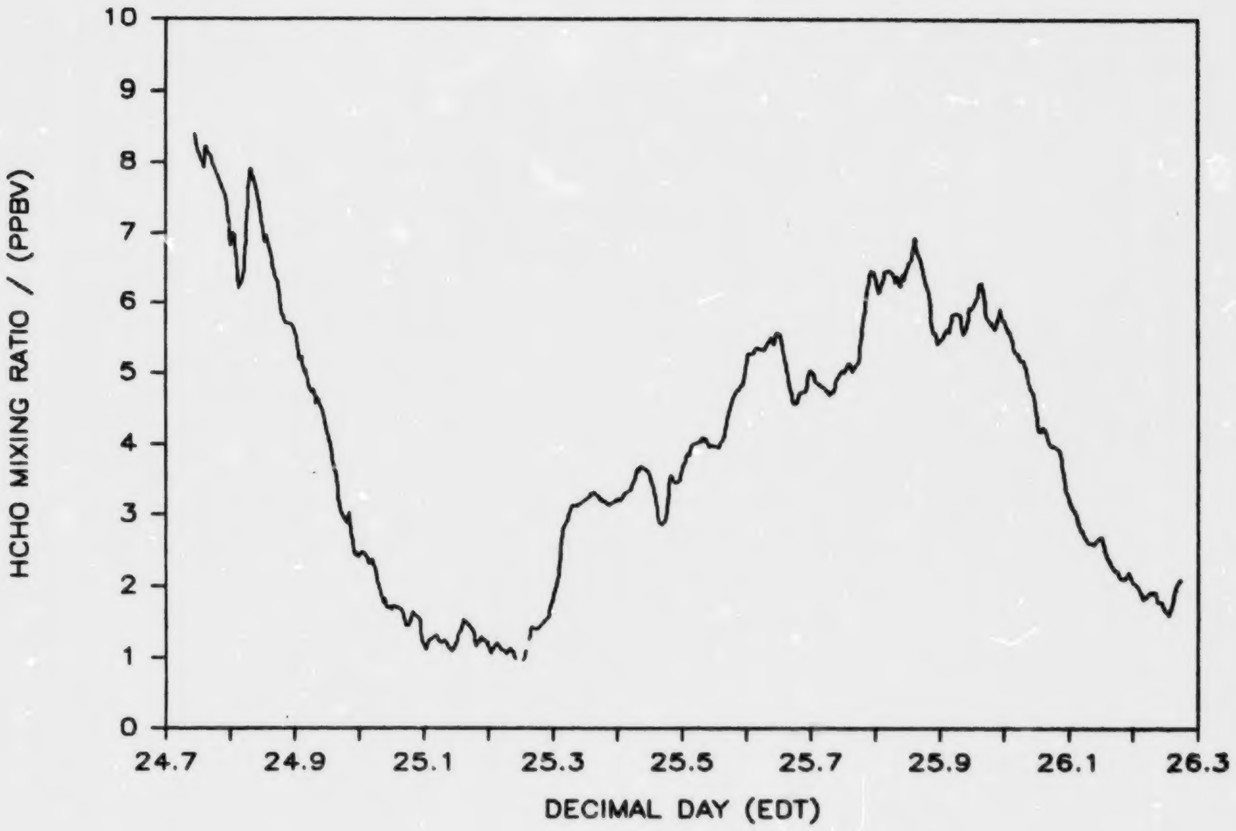


Fig 11: hourly average HCHO mixing ratios at Rayleigh NC.
Times shown are decimal days between June 24 and June 26.

Uptake, Distribution and Clearance of Soluble Aerosols from the Human Respiratory System

J.F. Hicks[1] and W.J. Megaw[2]
[1] AERE Harwell, Oxfordshire, U.K.
[2]York University, Toronto, Canada

In humid atmospheres, soluble aerosols may grow in size as water vapours condense upon the particle surfaces. The growth of soluble aerosols in the humid environment of the respiratory tract will affect the degree and site of deposition in the lungs. Once deposited, the soluble aerosols are subject to different clearance mechanisms than insoluble particles, and the residence times of such particles in the lung may be very short. Since it has been shown that most of the ambient aerosol is hygroscopic (Hicks and Megaw, 1985), this has a direct bearing on the estimation of health effects due to airborne pollutants. This paper describes a study of the growth, deposition, uptake and clearance for two different soluble aerosols, mainstream cigarette smoke and sodium chloride.

Effect on growth on total deposition

The sodium chloride aerosol was generated from a saline solution in a nebulizer (Acorn, Medic-aid Ltd., London). The aerosol was allowed to dry in a 40 litre glass chamber prior to inhalation. The size distributuion of the aerosols in the chamber was determined using a quartz crystal microbalance cascade impactor (QCM, Berkely Instruments, Model C1000-A) immediately before the subject inhaled 1 litre of the aerosol-laden air from functional residual volume. The exhaled air was diluted with dry air and sampled. Inhaled and exhaled aerosol measurements were used to determine the total lung deposition as a function of size for the NaCl aerosol. This procedure was repeated using mainstream smoke drawn from a lit cigarette using a syringe, and injected into a 40 litre glass chamber. The smoke was aged for approximately 1 minute before inhalation.

The results of the experiment conducted in 5 subjects were similar for both aerosols. The point of minimum deposition occurred at 0.1 um in contrast to 0.5 um for insoluble particles (Fig. 1). This minimum agrees with the results of others using NaCl (Blanchard and Willeke, 1983, Tu and Knutson, 1984), and with a model of NaCl deposition by Xu and Yu (1985). The results of Dautrebande and Walkenhorst (1961) record a smaller particle size of minimum deposition at 0.07 um. However this appears to be an optical diameter measurement and would equate to 0.09 um if the density of NaCl is considered.

Although the shape of the deposition curve matches past results, we found a large degree of inter-subject variability, and generally higher values of deposition than previously reported. This may be due to the subjects used or to the fact that our results are the only measurements of this type based on a mass measurement device instead of an optical particle counting method.

Since the deposition data indicated that small particles grow to larger sizes in the lung, a second experiment was conducted to determine the degree of aerosol growth in the respiratory tract. A direct measurement of the size distribution of the humidified, exhaled aerosol was taken at the mouth and compared with the aerosol after it had been dried, again using the QCM cascade impactor. For the humidified profile, the size distribution was measured one stage at a time and composite profile, was constructed from individual measurements. The time from exhalation to impaction was estimated to be less than 0.1 seconds, therefore little drying or cooling occured. The dry aerosol profile was measured once a sample of exhaled air had been dehumidified with dry air. This measurement was taken with the cascade impactor set in the normal mode and was not a stage by stage composite sample. The exhaled NaCl aerosol was found to be 4.5 times larger in mass mediam aerodynamic diameter when humidified than when dired. This growth is similar to that estimated by Ferron (1977). The humidified mainstream smoke measured 1.7 times larger than the dry size, yet with a similar minimum in deposition to NaCl.

Effect of growth on regional deposition

The regional deposition of both aerosols was investigated using a radioactive label, 1-iodohexadecane (I-123, $T_{1/2}$= 13.5 hr.) previously developed from mainstream smoke (Pritchard and Black, 1984). This was adapted to label NaCl by adding it to an ethanol-NaCl solution in the nebulizer. Upon nebulizing, the alcohol evaporates and the label is retained with the dry NaCl particles. The label constitutes less than 2% of the mass of the particle and did not appear to impede the condensation of water on the particle. Although both aerosols are polydisperse the size distributions are similar.

Table 1: Summary of Regional Deposition Experiments

Ref	Material	Tidal Volume l	Flow l s^{-1}	Pause s	Breathing rate min^{-1}	MMAD um	σ_g
1	40 ml puff of smoke	0.5	0.5	2	-	0.6	1.8
2	40 ml puff of smoke	1.5	0.5	2	-	0.6	1.8
3	260 ml smoke in 40 l	1.5	0.5	2	7	0.6	1.8
4	0.8 mg NaCl in 40 l	1.5	0.5	2	7	0.7	1.9

In the first two tests the volunteer drew a 40 ml bolus of labelled smoke from the cigarette. The bolus was then inhaled in a particular breathing regime (see Table 1). In the third and fourth tests the aerosol was inhaled from the 40 litre chamber over a period of 7 breaths. Five volunteers smokers were used in the experiment. After inhalation, lung retention was followed for 30 hours using the whole-body monitoring techniques previously developed (Pritchard and Black, 1984). Retention of the label in the lung can be described by a two-phase exponential, which may be interpreted as clearance from the tracheobronchial (TB) and pulmonary (P) regions. The P and TB components of the lung deposit were estimated by a weighted least squares technique which extrapolated the two phases of the retention curve back to the time of administration (Fig. 2).

The fraction of the lung deposit in the TB region is given in Table 2. The values for the deposition of cigarette smoke are in good agreement with those previously reported (Pritchard and Black, 1984). As can be seen, there is a large and consistent inter-subject variability. The use of a non-parametric ranking test (Friedman, 1937) shows that the subjects, as well as the experiments, cannot be considered as coming from the same sample population ($p < .025$ and $p < .01$ respectively) Experiments were compared using a paired t-test.

Two effects of breathing pattern on deposition were demonstrable. There was a decrease in the relative proportion of TB deposit on increasing the tidal volume ($p < .05$). This is due to the longer residence time of the aerosol deep in the lung resulting in increased deposition by sedimentation in the P region. Also, there was an increase in TB deposition during steady-state smoke inhalation when compared to a puff inhaled in the same manner. Presumably, this is because the bolus of smoke from a puff is swept into the P region by clean air wheras smoke is constantly present in the conducting airways during steady-state breathing, resulting in greater deposition by sedimentation in this region.

Table 2: Percentage of Tracheobronchial To Total Lung Deposits (%)

	Experiment			
Subject	1	2	3	4
A	81.9	80.7	82.2	84.6
B	69.3	63.3	69.1	78.5
C	61.7	57.7	72.4	72.8
D	55.4	53.9	56.2	54.2
E	46.3	45.4	65.1	53.7
Mean	62.9	60.2	69.0	68.8
+/- SE	6.1	5.9	4.3	6.3

Significant Conclusions of the Regional Deposition Experiment

Of primary importance is the signficant amounts of tracheobronchial deposition in every experiment. The amount of TB deposition found with insoluble particles in other experiments was much smaller. The soluble aerosols used in this experiment have deposited in this region to such a degree that the tracheobronchial component usually exceeds the pulmonary.

Table 3

Summary of Parameters by Volunteer

(Average of 7 Regional Deposition Tests)

	1	2	3	4	5
Average % P	18	32	31	49	52
Average % TB	82	68	69	51	48
Average P $t_{1/2}$ (hrs)	15.8	16.9	12.6	12.8	11.6
Average TB $t_{1/2}$ (hrs)	1.9	1.7	1.8	1.4	1.3
Average M $t_{1/2}$ (hrs)	12.9	12.5	10.7	11.3	11.5
Average Total Activity Absorbed (counts)	2097	2478	3552	2920	2650

The TB deposit was cleared very rapidly in all cases (average TB $t_{1/2}$= 1.6 hours) and most of the deposit was cleared within five to six hours. The deposit was cleared to the gut and some components entered the bloodstream from this point. Therefore, many soluble aerosols (e.g. air particulate) may deposit heavily in the tracheobronchial region, and be cleared to the gut and/or bloodstream within a few hours. The physical insult to the airway passages may only be present for a few hours, but if toxic components exist and are not digested by gastric juices they may still make their way into the bloodstream once cleared from the lung.

On the basis of these experiments we cannot assume most deposited submicron particles will reside in the pulmonary region. However, the degree of deposition varies from volunteer to volunteer and the tracheobronchial component may consist of 35% to 85% of the lung deposit. The determining factor appears to be highly dependent on the individuals' anatomy and breathing behaviour.

The degree of deposition appears to be dependent primarily on the length of time of breath. The longer the residence time of the aerosol in the lung the greater the deposit. Therefore the aerosol deposits via a time dependent mechanism, presumably sedimentation and diffusion.

It was noted that pulmonary deposition increased when the tidal volume changed from 0.5 to 1.5 litres. Also, the tracheobronchial component was greater in the multiple breath experiments than in the single breath "bolus" experiments. Presumably this was due to the deposition, via sedimentation, of smoke during respiratory "pauses".

The pulmonary clearance rate for this label was quite rapid. Instead of clearing over a period of months or years as insoluble substances do, this label had a half-life clearance rate of 10-20 hours. The rate depends on the individual and in this set of volunteers there appreared to be a dependence on age and/or smoking history. Periodic measurements on a larger number of volunteers over a period of years could explain why the pulmonary clearance rate varies from volunteeer to volunteer.

Although the regional despostion of mainstream smoke was not identical to that of the sodium chloride aerosol (Test #3 vs. Test #4 - Table 2), the deposition measurements of the two are comparable. The range in percent pulmonary deposition measurements for mainstream deposition (Test #3) was 18-44% (Ave. 31.8%) for the sodium chloride aerosol. Therefore the deposition measurements of the two aerosols are not dissimilar. Indeed, for a study that must use human volunteers the results are remarkably close.

It is also interesting to note that the total deposition measurements revealed a similar deposition curves for both the mainstream and sodium chloride aerosols. The two curves had similar points of minimim deposition at a particle size of 0.1 um (diameter). However, the degree of deposition did vary between the two aerosols.

Applicability of These Results of the Assessment of Environmental Particulate Deposition

The solubility of environmental particulate has been shown to be similar for many regions in the Province of Ontario. The total mass of the fine particulate has been found to be on average 60% soluble. Individual elements may differ widely in solubility but tend to show similar values from region to region in the province. Although the solublity of an element may be consistent from region to region, the total quantity of that element found airborne varies depending on the airshed being assessed.

An assessment of the size distribution of the fine particulate found it to be similar to that of the mainstream ciga re*te smoke used in these deposition and growth stuides. The D_{50} of the fine particulate was approximately 0.7 um with a sigma-g of 1.8 whereas the mainstream smoke had a D_{50} of 0.6 and a sigma-g 1.7. Similarly the mainstream smoke was found to grow in the presence of humidity by a factor of 1.7. The data of Hicks (1984) translates to a growth factor of environmental particulate of 1.8

Therefore, environmental particulate should undergo mechanisms of deposition and clearance in the lungs, similar to those of the mainstream cigarette smoke. It is likely that large portions of the inhaled particulate will deposit in the tracheobronchial tract as well as the pulmonary region. The deposited particulate should clear from the tracheobronhical tract to the gut within hours. Soluble elements will also pass from the gut into body fluids. Similarly many of the soluble particulate components should clear from the pulmonary region by absorption into the body. The pulmonary absorption route should drastically reduce the particulate burden in the lung within a few days after deposition. Other insoluble species most probably remain in the pulmonary region to be cleared by other means (e.g. macrophage long-term clearance).

Using the data obtained on fine particulate solubility we can identify some of the elements which will clear rapidly by absorption, and others which may build-up in the pulmonary region over long periods of time (See Table 4).

If we assume these elements do not react with the lung surface and that soluble elements will move through the epithelial layer as the tracer did regional deposition experiment, then we can determine the elements which are retained in, or cleared from the pulmonary region.

Table 4: Summary List of Elemental Solubility in Ontario Fine Particulate

Element	Percent Solubility
Aluminum	55
Silicon	21
Phosphorus	78
Sulphur	93
Potassium	88
Calcium	67
Titanium	8
Vanadium	56
Chromium	25
Manganese	65
Iron	14
Zinc	59
Bromine	74
Lead	70

Most of the inhaled silicon, titanium, chromium, and iron that deposits in the pulmonary region will be relatively insoluble. Hence it is unlikely they will absorb readily into the body fluids, but instead remain in the pulmonary aveoli, to be cleared by macrophages. These elements will be subject to long term clearance mechanisms.

However, other elements are primarily soluble and should absorb into the body fluids if deposited in the pulmonary region. These elements should almost completely absorb within days of being inhaled.

Certainly, most elements cannot be classified as completely insoluble. More likely each element has an insoluble and soluble fraction. It is also important to note that different geographical areas will have different levels of particulate elements in the air. For example the air in Area A of an Ontario city has an average silicon content of 0.9 ug/m^3 whereas Area B has an average of 0.15 ug/m^3 Si in the air. Therefore particulate levels must also be taken into account when assessments are made.

Some elements may be toxic to certain body tissuses. For instance, the element lead affects the nervous system and may be absorbed by the bones. Therefore the rate at which lead is absorbed from the lung and carried to these tissues may be important to its toxic assessment.

Particulates that deposit in the tracheobronchial region should be cleared in a matter of hours. However, these elements may be absorbed through the gut and may end up in the body fluids despite their rapid removal from the lungs.

In summary, particulate solubility is important to the assessment of xenophobic substances inhaled into the body. The solubility of a species may determine its rate of transport from sytem to system. Or it may be useful in calculating the long term build-up of insolubles in the lower lung.

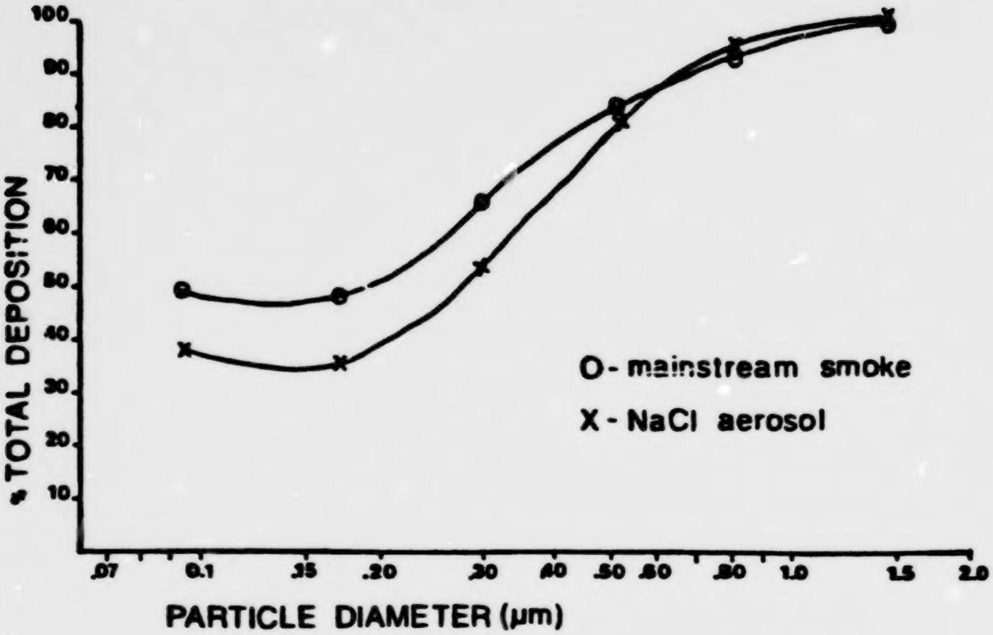


Fig. 1: Total deposition as a function of particle size for two soluble aerosols

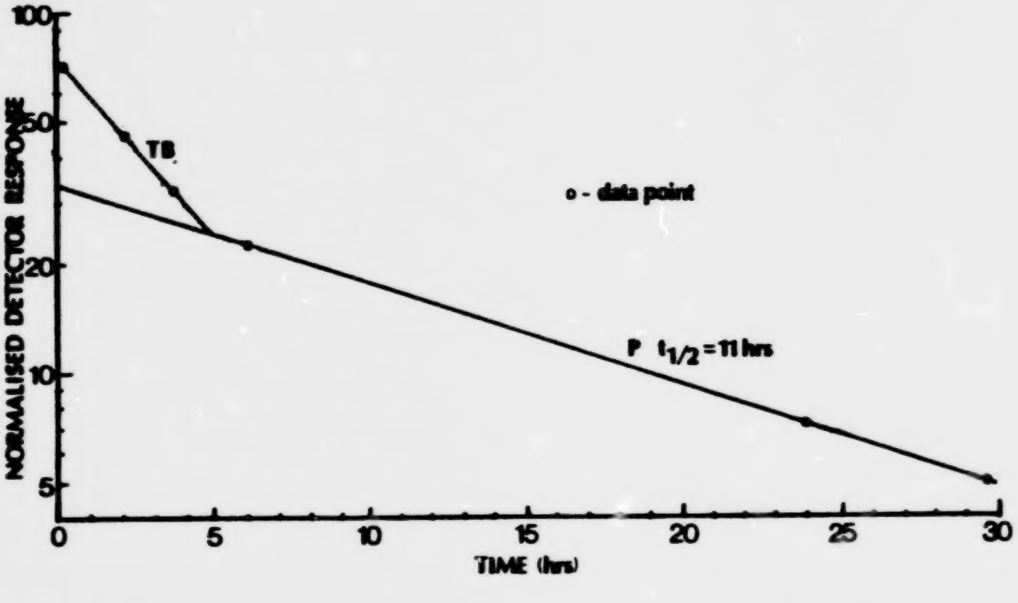


Fig. 2: Two stage chest clearance curve typically found in regional clearance experiments.

Blanchard, J.D. and Willeke, K. (1983) "An inhalation system for characterising total lung deposition of ultrafine particles." Am. Ind. Hyg. Assoc. J. 44:46.

Dautrebande, L. and Walkenhorst, W. (1961) "Deposition of NaCl microaerosols in the respiratory tract." Arch. Environ. Health 3:411.

Ferron, G.A. (177) "The size of soluble aerosol particles as a function of the humidity of air. Application to the human respiratory tract." J. Aerosol Sci. 8:251.

Friedman, M. (1937) "The use of ranks to avoid the assumption of normality implicit in the analysis of variance. "J. Amer. Statist. Assoc. 32:675.

Hicks, J.F. and Megaw, W.J. (1985) "The growth of the ambient aerosols in the conditions of the respiratory system" J. Aerosol Sci. 16:521. Hicks (1984) MSc. Thesis p. 110.

Pritchard, J.N. and Black, A. (1984) "An estimation of the tar particulate material deposition in the respiratory tracts of healthy male middle-and low-tar smoklers" in Aerosols (Edited by Lui, Pui and Fissan), Elsevier, New York.

Tu, K.W. and Knutson, E.O. (1984) "Total deposition of ultrafine hydrophobic and hygroscopic aerosols in the human respiratory system" Aerosol Sci. Technol. 3:453.

Xu, G.B. and Yu, C.P. (1985) "Theoretical lung deposition of hygroscopic NaCl aerosols" Aerosol Sci. Technol. 4:455.

6CPT6

EXPERIMENTALLY DETERMINED MUTATION RATES AS AN AIR QUALITY STANDARD: EFFECT OF IN VIVO ADMINISTRATION OF CARCINOGENS ON MUTATION FREQUENCIES IN PULMONARY CELLS

D.B. Couch, A. Bouch, H.K. Kaul, J.D. Gingerich,
K. Jain, and J.A. Heddle,
Department of Biology,
York University,
Toronto, Ontario M3J 1P3

ABSTRACT:

One health hazard arising from exposure to air pollution is respiratory tract cancer. The central role played by mutation in oncogenesis suggests detection of mutations induced in the cells at risk could provide a biological basis for establishing air quality standards. An assay to detect mutations arising in vivo in lung and tracheal epithelial cells is under development. To permit the use of cells which are difficult to clone, the assay utilizies autoradiographic detection of diphtheria toxin (DT)-resistant cells isolated from Chinese hamsters. Reproducable increases in the mutant frequency have been detected routinely, but these have been small, about three-fold, even though a potent lung carcinogen (urethane) and a potent mutagen (ethyl nitrosourea) were used. This contrasts with the 50-100 fold increases readily induced in Chinese hamster ovary cells by potent mutagens. Although mutation to DT-resistance can be readily induced in cultured Chinese hamster ovary (CHO) cells and the resistant cells detected autoradiographically, only small, approximately three-fold, but reproducible, increases in the frequency of DT-resistant pulmonary epithelial cells from animals exposed to a potent lung carcinogen, urethane, or a potent mutagen, ethylnitrosourea, have been detected.

In an effort to elucidate the reasons for the differences in response, we have turned to the use of another cell type, lung fibroblasts, and genetic marker, resistance to the purine analog 8-azaguanine. Treatment of Chinese hamsters with ethylmethanesulfonate or diethylnitrosamine results in a dramatic increase in the azaguanine-resistant fraction of isolated lung fibroblasts. In vitro treatment of these primary lung fibroblasts with ethylmethanesulfonate also induces large increases in the frequency DT-resistant cells. These results indicate that the failure of the autoradiographic assay to detect large increases in the frequency of DT-resistant pulmonary cells following in vivo exposure to mutagens is not due to factors such as ineffective in vivo dose levels, greater repair capacity in vivo, or a refractory genome. Work is in progress to determine if the in vivo results with DT-resistance is an artifact of the isolation procedure, as seems likely. If so, identification and elimination of it could lead to the desired increase in sensitvity of the autoradiographic assay. As an alternative approach, the use of a mutational assay using azaguanine-resistance in primary lung fibroblasts to detect pulmonmary carcinogens is also being explored.

INTRODUCTION:

A quantitative assay for the toxic effects of airborne contaminants that is both relevant and inexpensive would be useful in establishing air quality standards. We are developing such an assay for carcinogenic air pollutants based on measurements of mutation in lung and tracheal cells in test animals. Most existing mutational assays are based on the ability of mutant cells to form colonies under selective conditions, but the difficulties in cloning pulmonary epithelial cells led us to consider alternate approaches, in particular the use of resistance to diphtheria toxin (DT) as a marker. Since DT exerts its toxic effect on cells by inhibiting protein synthesis (reviewed in Pappenheimer, 1977), individual cells which can incorporate radio-labelled amino acids into protein after exposure to DT can be identified by autoradiography. The feasibility of identifying DT-resistant cells by autoradiography has been demonstrated in vitro in cultured Chinese hamster ovary cells (Ronen et al., 1984) and human dipoid fibroblasts (Gupta and Singh, 1985), although the technique does not appear to be applicable to human lymphocytes (Tompkins et al, 1985).

We have previously reported the development of methods for the isolation and culture of epithelial cells of the lung and trachea of Chinese hamsters (Heddle et al., 1985). Although these culture conditions do not readily allow cell growth, especially of lung cells, cells can be maintained in culture for up to two weeks and are suitable for measurement of DT-resistance. Further, audioradiographic procedures have been adapted for use with these cultures. We report here that the effect of in vivo administration of mutagens and carcinogens on the frequency of DT-resistant lung and tracheal cells and on further development of an in vivo/in vitro somatic cell mutational assay utilizing pulmonary cells.

MATERIALS AND METHODS:

The DT used in these studies was purchased from Connaught Laboratories (Toronto, Ontario). Urethane, ethylnitrosourea and azaguanine were obtained from Sigma Chemical Company (St. Louis, MO). Cell culture medium, trypsin and cell culture dishes were purchased from GIBCO Canada (Burlington, Ontario); fetal boving serum was purchased from BDH Chemicals (Toronto, Ontario). Tritiated leucine [L-(4,5-3H)-leucine, 1.92TBq/mmole] was obtained from Amersham Corporation (Oakville, Ontario) and NTB-2 emulsion and D-19 developer from Eastman Kodak Company (Brampton, Ontario).

The Chinese hamsters (5-6 weeks old when purchased from Cytogen Research and Development , Inc., West Roxbury, MA) used through out these studies were maintaned under the guidelines of the Canadian Council of Animal Care. Animals were housed in 20 degree rooms at 50% relative humidity in a 12-hour light-dark cycle. Hamsters were kept in wire cages with wood-chip bedding and given free access to food (Purina lab chow) and water.

Animals were treated with solutions of carcinogens (or vehicle alone) by intraperitoneal injection. After various times were allowed (see RESULTS) for in vivo expression of the mutant phenotype, animals were killed and the lung and/or tracheal epithelial cells removed and maintained in culture as previously described (Heddle et al., 1985). Lung cells from indivdual animals were used to determine the DT-resistant fraction, whereas it was necessary to pool tracheal cell from three animals to provide sufficient cells for the measurement. After 24 hours in culture to allow attachment to culture dishes, cells were treated with toxin. Various combinations of DT concentration and treatment time have been tested and are described below. After intoxication, cells were incubated with 3H-leucine and prepared for autoradiographic examination as previously described (Heddle et al., 1985)

In some studies, primary cultures of fibroblasts isolated from the pulmonary tissue of Chinese hamsters were employed to measure both DT-resistance (by autoradiography) and 8-azaguanine(AG)-resistance (by a clonal assay). The treatment of the animals, the isolation and culture of the fibroblasts, and the assay for AG-resistance were performed as described by Dean and Senner (1977).

RESULTS AND DISCUSSION:

In order to determine whether treatment with carcinogens could increase the frequency of DT-resistant pulmonary epithelial cells, hamsters were treated with urethane (ethyl carbamate), known to induce lung tumors when administered to experimental animals by various routes, including intraperitoneal injection, to experimental animals (Shimkin and Stoner, 1975). As these experiments were intended as a demonstration of the feasibility of the approach, as well as to refine the selective conditions and provide preliminary information on the time required to express the DT-resistant phenotype in vivo, high doses of urethane were employed. Animals were treated with 1g/kg urethane daily for six successive days and sacrificed six days after the last injection. Lung and tracheal cells were treated with 100 LF/ml DT for up to 72 hours. The labelling indices (+ DT) of control animals, while considerably higher than found in CHO cells, are in good agreement with that reported previously (Heddle et al., 1985). At the most stringent selective conditionds employed, urethane produced only a three-fold increase in the DT-resistant fraction of tracheal cells and was even less effective in the lung (Table 1). Reducing the DT concentration to 1 or 10 LF/ml produced essentially the same result (Table 2).

TABLE 1. EFFECT OF IN VIVO ADMINISTRATION OF URETHANE ON THE FREQUENCY OF DT-RESISTANT LUNG AND TRACEA CELLS

Time of Exposure to DT (h)	Frequency of DT-Resistant Cells (x 10^3)		
	Control	Urethane (6x)[1]	Urethane (3x)[2]
Lung			
16	4.0	3.7	5.6
24	1.3	2.7	3.6
36	1.0	1.9	2.5
72	0.6	1.1	1.2
Trachea			
16	4.2	3.8	4.2
24	2.4	2.9	2.8
36	0.8	1.6	2.4
72	0.3	1.1	1.0

[1] Animals received 6 daily intrapertoneal injections of urethane (1g/kg) and were sacrificed 6 days after the last treatment.

[2] Animals received 3 injections of urethane at 3 day intervals and were sacrificed 3 days after the last treatment.

TABLE 2. EFFECT OF DT CONCENTRATION ON FREQUENCY OF DT-RESISTANT CELLS IN CONTROL AND URETHANE-TREATED ANIMALS

Concentration of DT[1] (LF/ml)	Frequency of DT-Resistant Cells (x 10^3)		
	Control	Urethane (6x)[2]	Urethane (3x)[2]
Lung			
1	1.3	1.9	2.8
10	0.9	1.6	1.7
100	0.6	1.1	1.2
Trachea			
1	0.5	1.2	0.8
10	0.3	1.2	1.3
100	0.3	1.1	1.0

[1] Cells were incubated in DT for 72h.
[2] Animals were treated with urethane as described in Table 1.

As the efficacy of urethane as a lung carcinogen may not be entirely due to its mutagenic potency, animals were treated with N-ethyl-N-nitrosourea (ENU), an extremely potent mutagen in vitro or in vivo (cf. Natarajan etal., 1984; Russell et al., 1979). Hamsters were treated with 160 mg ENU/kg body weight and allowed 2-10 days expression time. The DT-resistant fraction of tracheal cells increased up to 6 days expression time, but again there was only a relatively small (approximately 4-fold) increase relative to control. Treatment with ENU did not affect the DT-resistance of lung epithelial cells (Table 3). Higher doses of ENU (up to 340 mg/kg, a dose which is fatal to 50% of the animals receiving it) were not effective

TABLE 3. TIME REQUIRED FOR IN VIVO EXPRESSION OF DT-RESISTANCE IN LUNG AND TRACHEAL CELLS

Expression Time[2] (days)	Frequency of DT-Resistant Cells ($x 10^3$)[1] Lung		Trachea	
	Control	ENU	Control	ENU
2	0.5	0.6	0.2	0.5
4	0.5	0.6	0.2	0.7
6	0.6	0.5	0.3	1.3
8	0.5	0.8	0.3	1.3
10	0.5	0.9	0.3	1.5

[1] Isolated lung and tracheal cells were incubated with 100 LF/ml DT for 16h prior to labelling with ^{3}H-leucine.

[2] Animals were treated by intraperitoneal injection with 160 mg ENU /kg body weight (or solvent alone) and sacrificed at the time indicated after treatment.

in producing furhter increases in the labelling index of tracheal cells, nor did they increase in the fraction of DT-resistant lung cells (Table 4).

If the high spontaneous frequency of cells which can incorporate tritiated leucine after DT treatment is not be due solely to the mutant fraction of those cells, increases in the frequency of DT-resitance due to mutation may be obscured. Attempts were made to improve the stringency of the selction by incorporating a brief (20

TABLE 4. EFFECT OF ENU DOSE ON THE FREQUENCY OF DT-RESISTANT LUNG AND TRACHEAL CELLS

Dose ENU	Frequency of DT-Resistant Cells (x 10^3)	
(mg/kg)	Lung	Trachea
0	0.5	0.4
160	0.6	1.3
240	0.3	0.3
320	0.3	0.3

Animals were treated with ENV by intraperitoneal injection and allowed 6 days to express the mutant phenotype. Selection for DT-resistance was at 100 LF/ml DT for 72h.

minute) exposure to slightly acidic conditions (pH 4.4-6.8), which has been reported to enhance the cellular uptake of diphtheria toxin (Sandvig and Olsnes, 1980). Although exposure of cells to pH 6.0 buffer before intoxication did result in a substantial decline in the labelling index of cells from untreated animals, it also abolished the response induced by urethane (Table 5). Attempts have also been made in CHO cells to improve the stringency of the selection by incorporating exposure of the cells to toxin at temperatures which are not conducive to protein synthesis, but these attempts have not proven successful (data not shown). This method of increasing the responsiveness of the assay was thus abandoned.

TABLE 5. EFFECT OF pH ON THE LABELLING INDICES (+DT) OF LUNG AND TRACHEAL CELLS

	Frequency of Labelled Cells (x 10^3)[1]	
pH	Lung	Trachea
4.4	-	-
4.8	1.5	0.2
5.2	2.6	0.2
5.6	3.8	0.7
6.0	1.2	0.4
6.4	0.9	0.4
6.8	1.1	0.3
7.2	4.5	0.6
7.4	4.8	0.7

[1] Cells were maintained in culture 24h after isolation, then exposed to buffer at the indicated pH. The buffer solution was removed and centrifuged to collect any cells which may have detached. These cells were returned to the dishes in medium containing 100 LF/ml D+ and incubation continued for 72h.

Although there were indications that mutations leading to DT-resistance could be detected by an autoradiaographic assay with tracheal epithelial cells, at least, the sensitivity of the procedure was not sufficient to permit its proposed use in establishing air quality standards. Many possible explanations could be devised for the observed findings, and, to help establish which of these may be correct, we turned to the use of another genetic marker, resistance to 8-azaguanine. Dividing cells are required for this procedure so subsequent studies were performed on primary lung fibroblasts isolated from Chinese hamsters.

We first asked whether mutations can be induced in somatic pulmonary) cells in vivo by known carcinogens and mutagens. In agreement with the results of Dean and Senner (1977), treatment of Chinese hamsters with ethylmethansulfonate (EMS) or N-nitrosodiethylamine (DEN). was found to produce a dose-related increase in the AG-resistant fraction of primary lung fibroblasts (Table 6). Although the AG-resistant mutants were induced in fibroblasts and the DT-resistant mutants were induced in epithelial cells, these two cell types are closely apposed in the lung. Thus these results indicate the lack of response observed with epithelial cells is probably not a result of failure of the test compounds to reach pulmonary tissues in sufficiently high concentration to produce an effect, nor does it appear that the discrepancy in results obtained with the autoradiographic assay in CHO and pulmonary epithelial cells can be attributed to more efficient repair of mutagenic lesions in vivo or to a generally lower induced mutation rate in vivo than in established cell lines. It could be, however, that fibroblasts used in the clonal assay differ in these particulars from epitheial cells used in the autoradiographic assay.

We then asked if the failure to detect mutation to DT-resistance in vivo was a consequence of the genetic character of the cells exposed to toxin. It could be that hemizygosity of CHO cells allows

TABLE 6. EFFECT OF IN VIVO ADMINISTRATION OF EMS AND DEN ON THE FREQUENCY OF 8AG-RESISTANT PRIMARY LUNG FIBROBLASTS

Dose (mg/kg)	Mutant Frequency[1] ($\times 10^4$)
EMS	
0	< 0.3
50	< 0.4
100	1.1
200	2.4
400	6.8
DEN	
0	0.1
250	2.6
500	3.9
1000	6.1

[1] Animals were treated with EMS and DEN but intraperitoneal injection; after treatment fibroblasts were isolated 5h after treatment and the 8AG-resistant fraction determined 5h later, according to the method of Dean and Senner (1977).

recessive mutations to be detected that would not be evident in diploid cells. Accordingly, freshly isolated lung fibroblasts were treated in vitro with EMS, and the DT-resistant fraction determined following five days in culture. A marked increase in the mutant fraction over control was obtained (Table 7), indicating the

TABLE 7. EFFECT OF IN VITRO ADMINISTRATION OF EMS ON THE FREQUENCY OF DT-RESISTANT PRIMARY LUNG FIBROBLASTS

Time[1]	Frequency of DT-Resistant Cells ($x 10^6$)	
(days)	Control	EMS[2]
4	9.2	240
7	2.6	210
14	0.6	200

[1] Fibroblasts were isolated and maintained in culture for the indicated time prior to treatment with EMS.

[2] Cells were treated with 250 ug/ml EMS for 20h and then maintained in culture for 5 days before exposure to 100 LF/ml DT for 16 hours. Resistant cells were detected autoradiographically.

autoradiographic assay is suitable for use with hamster diploid cells (as it is for diploid human fibroblasts; Gupta and Singh, 1985). In one experiment, however, ultraviolet irradiation of primarly lung cells did not increase the labelling index of fibroblasts in the presence of DT (data not shown).

Preliminary results indicate that treatment of Chinese hamsters with EMS does not appreciably increase the DT-resistant fraction of lung fibroblasts isolated from the animals soon after treatment and allowed to express the mutant phenotyupe in vitro for five days, although 8-azaguanine-resistance is increased in another cohort of the same cell population. If these results are confirmed, it will suggest that the failure of to detect DT-resistant fibroblasts, and possibly epithelial cells as well, following in vivo administration of mutagens, is an artifact arising from the isolation procedure. Alternatively, there may be differences in the response of fibroblastic and epithelial cells to mutagens in vivo. This possibility is under investigation using a clonal assay for azagunanine-resistant tracheal cells to compare their response to that of pulmonary fibroblasts.

CONCLUSIONS

Optimal conditions for detecting DT-resistant epithelial cells of the lung and trachea have not yet been found, but recent findings suggest that the problems encountered may arise as an artifact of cell isolation and are not a failure to induce mutations in the target cells. The ease with which AG-resitant lung fibroblast can be detected offers another approach to detect potential pulmonmary carcinogens, which is also being actively pursued.

REFERENCES

Dean BJ, Senner KR (1977): Detection of chemically induced somatic mutations in Chinese hamsters. Mutat Res 46: 403-406.

Gupta RS, Singh B (1985): Autoradiographic detection of diphtheria toxin resistant mutants in human diploid fibroblasts. Environ Mutagen 7: 611-624.

Heddle JA, Jain K, Kaul H, Couch DB (1985): Experimentally determined mutation rates in lung and bronchial epithelial cells as a primary air pollution standard: method development. Proceedings of Technology Transfer Conference No. 6, Research Advisory Committee, Ministry of Environment, Ontario, Canada. Part 1, pp 98-106.

Natarajan AT, Simons JWIM, Vogel EW, vanZeeland AA (1984): Relationship between cell killing, chromosomal aberrations, sister chromatid exchanges and point mutations induced by monofunctuional alkylating agents in Chinenes hamster cells. Mutat Res 128: 31-40.

Pappenheimer AM (1977): Diphtheria toxin. Ann Rev Biochem 46: 69-94.

Ronen A, Gingerich JD, Duncan AMV, Heddle JA (1984): Autoradiographic assay of mutants resistant to diphtheria toxin in mammalian cells in vitro. Proc Natl Acad Sci USA 81: 6124-6128.

Russell WL, Kelly EM, Hunsiker PR, Bangham JW, Maddux SC, Phipps EL (1979): Specific locus test showes ethylnitrosourea to be the most potent mutagen in the mouse. Proc Natl Acad Sci USA 76: 5818-5819.

Sandvig K, Olsnes S (1980): Diphtheria toxin entry into cells is facilitated by low pH. J Cell Biol 87: 828-832.

Shuimkin MB, Stoner GD (1975): Lung tumors in mice: application to carcinogenesis bioassay. In Adv Cancer Res 21, S Weinhouse, A Haddow (eds.), Academic Press, NY, pp 223-267.

Tomkins DJ, Wei L, Laurie KE (1985): Diphtheria toxin resistance in human lymphocytes and lymphoblasts in the in vivo somatic mutation test. Environ Mutagen 7: 811-820 (1985).

THE HAMILTON STUDY: EFFECT OF FINE PARTICLES ON THE RESPIRATORY HEALTH OF SCHOOL CHILDREN

L. D. PENGELLY[1], C. H. GOLDSMITH[2], A. T. KERIGAN[1],
W. FURLONG[1] AND S. A. TOPLACK[1]

DEPARTMENTS OF MEDICINE[1], and CLINICAL EPIDEMIOLOGY
AND BIOSTATISTICS[2]

McMASTER UNIVERSITY,
HAMILTON, ONTARIO, CANADA

ADDRESS FOR CORRESPONDENCE:

Dr. L. D. Pengelly
Urban Air Environment Group
Room 3E27
McMaster University
Health Sciences Centre
Hamilton, Ontario
L8N 3Z5

*SUPPORTED BY: Province of Ontario: Ministry of the Environment
Ministry of Health
Canada : Health and Welfare

BACKGROUND

Early studies from our laboratory showed that the persistent aerosol in the atmosphere over Hamilton could be visualized and its extent and altitude measured by a simple technique using a searchlight (1). In this study we demonstrated that aerosols were frequently trapped in inversion layers over the city, especially when the wind came from the northeast over the cold lake.

We also operated a pollution sampling network between Lake Erie and Hamilton using Hi-Vol samplers for "Total Suspended Particulate" (TSP) and Andersen cascade impactors to measure particle size distribution (PSD). We were able to show that both the concentration and size of the particles moving from Lake Erie in the direction of the prevailing wind toward Hamilton increased substantially. The greatest increase began at the city limits, and substantial gradients were observed while moving in a northeasterly direction over the industrial area (2).

Thus before we started the present study, we had good evidence that there were substantial gradients of TSP and PSD the highest levels being more than twice the lowest levels. As a consequence, we decided to make use of these gradients to carry out an epidemiological study of the effects of air pollution on respiratory health.

METHOD

We decided to carry out our study by examining the effects of air pollution and other environmental factors on the respiratory health of a sample of elementary school children in the city of Hamilton. We were aware that many factors other than air pollution influenced respiratory health, so our study was set up to examine the relative contribution of many environmental factors on the respiratory health of our school children.

We chose to study children enrolled in schools of the Board of Education of the City of Hamilton in grades 2, 3 and 4 who had not reached their 11th birthday by December 31, 1978. There were over 8400 children in these grades, and sample size calculations indicated that we would require 3200 in a stratified random sample (5). An attempt was made to have the children uniformly distributed over 4 "quadrants" of the city (west upper - WU, east upper - EU, west lower - WL, and east lower - EL), as shown in Figure 1. Figure 1A shows the areas of the city, and the locations of the aerosol samplers. Figure 1B shows the distribution of the schools with respect to the samplers. In the second year (Year II) of the study (reported here), which took place in 1980, we added children of the same age as the original cohort from three schools in the industrial core (IC) of the city, a subsection of the EL quadrant. The total number of children studied in Year II was 3588. Parents were interviewed and children studied once each year for a total of three times, essentially in the calendar years 1979, 1980, and 1981. Further details of the sample are given in a previous report (5).

Measurements of Suspended Particles

For the purposes of the epidemiological study, we set up a pollution sampling network to measure TSP at 27 sites and PSD at 7-9 sites. At the time we began the study, the Ontario Ministry of the Environment (OME) operated 11 TSP sites in an abatement-oriented network in the industrial and commercial parts of the city, and had no ongoing measurements of particle size distribution. Since for our purposes we had need of an estimate of an exposure which was more population based, we found it necessary to complement the OME network with 16 TSP sites of our own, and to set up a network of PSD samplers (7 in 1979 and 1980, 9 in 1981). Our TSP sites were for the most part located in residential areas, but the PSD locations were distributed across the city.

TSP was measured with standard Hi-Vol samplers (General Metal Works GMWL-2000H) using glass fibre filter paper, and PSD was measured using the same housing, but with a 4-stage cascade impactor designed to operate at 20 cfm (Andersen 2000) (4). Flow recorders were used on all TSP samplers. PSD flow was set to 20 cfm before sampling by means of variable auto transformers on all PSD samplers, and was measured and recorded after sampling. Filters were conditioned at known humidity before and after exposure, and weighed with a Mettler Gram-matic balance. Both networks were operated every six days synchronously with the North American Synoptic Six-day Cycle. Quality control procedures were used, which will be reported elsewhere.

Summarization of Data

For TSP, the results for each site were expressed in ug/m^3, and this was recorded together with the site identification number and the date of sampling. The five or six values for a given site were used to generate a monthly geometric mean value for that site. If fewer than three values were available for a site for a given month, the data for that month were declared "missing". This criterion also held for PSD. In order to summarize the results of the measurements obtained by the PSD network, we chose to obtain monthly average values in the following way. Since the sampler collected aerosol on four separate impactor stages as well as on a backup filter, on a given sampling day we could measure it in each of five size ranges, and this was expressed in micrograms per cubic meter. To obtain a summary of information for a month, the loadings on corresponding filters were added together for the five or six sample days, and a mean monthly loading for each stage or filter was calculated. From the five monthly loadings, aerodynamic mass median diameter could be calculated in the standard manner and expressed as MMD in micrometers (um) (4). In addition, we decided to add the loadings of the first two stages together including particles greater than 3.3 um, and referred to this as the "coarse fraction" (CF). We added the loadings of the third and fourth stage as well as the backup filter together and referred to this as the fine fraction (FF) (i.e. that less than 3.3 um). Thus for a given month, we had a measure of MMD obtained from all the loadings for that month, and a measure of coarse and fine fraction which was obtained from the sum of the corresponding loadings for that month, and expressed as ug/m^3.

Analysis of Data from Air Pollution Networks

Our objective was to determine an exposure which was as closely as possible unique to each child in the study. For practical purposes we decided to use a time resolution of one month, and a spatial resolution determined by the location of the school the child attended at the time the child was tested. Thus we had need of a method by which we could estimate a monthly exposure on a school-by-school basis.

Using the monthly values obtained for each site for each variable (TSP, MMD, CF, FF), a response surface was calculated which expressed in three-dimensional terms (vertical direction -

aerosol variable; horizontal "x" - easting geographical co-ordinate; horizontal "y" - northing geographical co-ordinate) an estimate of the distribution of the aerosol as a function of the geographical plane of the city. For MMD, CF and FF the form of the response surface model was:

MMD = B0 + B1(E) + B2(N) + B12(EXN) + e

where MMD is the response value,
B0, B1, B2, and B12 are regression coefficients,
E and N are normalized easting and northing geographical coordinates, and
e is the error term

In addition, the coefficient of determination of the surface could be calculated, indicating the proportion of the variation in the data explained by the model we fitted. In most cases over 2/3 of the variability in the data was accounted for by the fitted model.

To calculate an exposure value for an individual child, an annual mean was determined by taking the arithmetic mean of monthly values of a given variable for the school location at the time of testing: for the month of testing, the 9 months preceding it, and the 2 months following it. The yearly average was used because we were looking for long-term or chronic effects both in respiratory symptoms and as indicators of these in pulmonary function, and because plots of yearly air quality measurements indicated that seasonal cycles repeated within the years.

Respiratory Health

The respiratory health of the children, and home environmental and socio-economic variables were assessed by means of a questionnaire administered to the children's parents. Pulmonary function tests were conducted in the schools after having received consent from the parents of the children. Interviews and tests were conducted once a year for a period of three years.

RESULTS

Suspended Particles

Figure 2 shows contours of mass median diameter obtained using the response surface model for the month of May 1980. Each small number which defines the contour line represents twice the mass median diameter defined by that line; i.e., "8" = 4 um MMD. The particle size to which the children were exposed was calculated on the basis of monthly maps of this type.

We found that the pattern of the distribution of particle size and fine and coarse fraction was similar from year to year, as is shown in Figures 3 and 4. Figure 3 shows the calendar yearly response surface contours for the three years 1979, 1980 and 1981. Although the nature of the contours are determined in part by the model, it is apparent that the shapes of the contours are similar from year to year. The southwest-northeast axis of symmetry probably relates to the two dominant wind directions: southwest (35% of the time) and northeast (11% of the time) (4). It is clear from these contours that a substantial gradient exists over the city. In Figure 4, the numbers on each contour represent tens of micrograms per cubic meter. For the years 1979 and 1980 the patterns are quite stable, with substantial gradients in both fractions. In 1981 however, when a recession and a prolonged steel strike reduced industrial activity, the reduction in the gradient for the coarse fraction was much more marked than that seen for the fine fraction.

Respiratory Health

In the year of the study being reported here (Year II, Jan. - Dec. 1980), a total of 3439 children had both a completed parental interview and a pulmonary function test session. The response rate for interviews was greater than 95% in all years, and the response rate for testing was greater than 92% for Years II and III, and greater than 89% in Year I.

Details of the prevalence rates for respiratory symptoms and the values of pulmonary function will be reported elsewhere. In this report, for the purposes of associating with the effects of particle size we have selected two indicators of respiratory health (cough, and episodes of bronchitis), and two indicators of pulmonary function, both adjusted for body size.

Several factors have previously been implicated in a reduction of respiratory health of children even without an effect of pollution. We have previously reported on this problem and the extent to which it might have influenced our data, and for that reason found it necessary to use a method of analysis which was more complex than the demonstration of simple independent associations (i.e. not adjusted for confounding factors) between health effects and air pollution (5).

Relative Strength of Environmental Effects

We chose to analyse these interdependent associations using stepwise multiple regression techniques. Initially we found a variety of independent variables that had shown at least one significant association with health-related outcomes. A list of these independent variables is given in Table I. We found, for example, that when examined as a single variable, gas cooking was associated with an increased prevalence of colds going to the chest. In the multiple regression analysis, all variables are introduced together and the computer selects the variables with the strongest and most significant effects, rejecting others that are highly correlated with the one selected. For continuous dependent variables, multiple linear regression was used; for binary dependent variables such as symptoms, the multiple logistic regression was used. A variable was said to be significant if the probability of a chance association was less than 0.05 (=0.05).

Symptoms

The results of the logistic regression for symptoms are shown in Table II. The logistic regression calculates the influence of an independent variable on the probability of occurrence of an outcome variable according to the function shown in the Table. For example, two independent variables that were found to be significantly associated with the probability of a child having a cough during the day or night were: maternal cough, and hospitalization as an infant with respiratory disease. All other factors included were not significantly associated. In the table, the "p" value relates to the probability of the association being by chance (not the probability of the cough). Also in the table it can be seen that the probability of a child having an episode of cough and phlegm lasting at least three weeks (bronchitis) was significantly associated with three factors, maternal smoking being added to the other two.

Pulmonary Function

One of the measurements frequently made in respiratory epidemiological surveys is that of Peak Expiratory Flow (PF). Since the magnitude of PF is dependent on the size of the child, we have adjusted the values to the mean height of all the children (APF). In the example shown in Table III, the first equation shows that APF is reduced with an increased magnitude of the fine fraction. In addition, if the child shares a bedroom APF would be further reduced. Only these two variables were found to have an effect on adjusted peak flow. The MEF 75 is also a function of body size and must be suitably adjusted. From Table III, it may be seen that AMEF75 is significantly affected by three factors: maternal smoking; hospitalization of the child as an infant; and increased particle size. The observation with respect to particle size (MMD) should probably be interpreted in another way, however. It would be more logical to expect a reduction in function associated with particle exposure, and thus it could equally be said that MEF75 is reduced with a reduction in particle size, which would be consistent with the findings for peak flow.

DISCUSSION

We have carried out a study of the effects of ambient aerosol pollution and other environmental factors on the respiratory health of over 3500 school children in an industrial city. We have demonstrated a substantial gradient in aerosol concentration and aerodynamic mass median diameter over the area in which the children live and attend school. By taking advantage of this gradient in exposure, and by assessing a variety of independent variables, we have shown that there are strong effects of the home environment, particularly of maternal smoking, and significant consequences of severe respiratory disease in infancy (which has been shown by others to be associated with smoking in the home) (6). We have also demonstrated effects of the fine fraction of aerosol pollution. Although this is based on a cross-sectional analysis of one year of data from the study, it is new evidence that the fine fraction of urban aerosol is associated with a degradation of pulmonary function in school children. There have been many studies of the effects of air pollution on the respiratory health of children (7-16), but only one has measured (but not yet reported) the effects of particle size (17).

We have previously reported that indices of the Forced Vital Capacity (FVC) have greater discriminatory power in separating children with symptoms from those without, compared to tests using nitrogen washout (18). For the purposes of this report we have included the results of measurements of two pulmonary function variables (PF and MEF75) adjusted for height. We also examined other indices of the FVC, such as FEV_1/FVC, and height-adjusted FEV_1, MMEF, and MEF50. Three tests (FEV_1/FVC, MMEF, and MEF 50) all showed an effect of early hospitalization, and maternal smoking. Two showed effects of particles, which were just significant at the 0.05 level; MMEF showed an association with TSP, and FEV_1 an association with MMD. Both associations were positive, suggesting the interpretation of a "fine particle effect", as we have evidence of a positive association between TSP and MMD. Thus the results of the other pulmonary function tests which we carried out are similar to those we presented in more detail, but the strength of the associations were less.

The same general points can be made about respiratory symptoms. The other symptoms that were examined, such as presence of any cough (not necessarily chronic), persistent wheeze, or colds "going to the chest" were all associated with hospitalization as an infant and maternal cough or maternal smoking. "Cold going to the chest" was associated with all 3 of the above, as well as concentration of TSP above the median (50 ug/m^3), but only at the 5% level. Symptoms were not associated with our measures of particle size.

SUMMARY

We have operated a network of Andersen 2000 cascade impactors in the industrial city of Hamilton, Ontario, Canada, and have demonstrated statistically significant gradients in particle size over the city. We have carried out at the same time in the same city an epidemiological study of respiratory health of over 3500 elementary school children in whom we have measured pulmonary function and the prevalence of symptoms, as well as characteristics of the home environment, including family smoking. We have developed a method of determining exposure of each child to particles which depends on the location of the child and the characteristics of the gradient we have observed. We found strong negative health effects of the home environment, particularly maternal smoking, and relatively weak effects of the ambient air quality. We did observe, however that there was a statistically significant association between decrement in pulmonary function and an exposure to fine particles.

ACKNOWLEDGEMENTS

We wish to acknowledge the support of the Province of Ontario, through the Ministry of the Environment (Project 78-020-33), and the Ministry of Health (Public Health Grant CHS-R34); and of Health and Welfare Canada, through their National Research and Development Programme (Project 6606-1752-53). We are grateful to the staff of the Urban Air Environment Group, Department of Medicine, for their dedicated work on this project, and to the Hamilton Opinion Research Centre Ltd. for obtaining the questionnaire data.

Table I. Independent Variables in Regression

- Hospitalization at < 2 Yr. of age for Respiratory Illness
- Mother Has Cough
- Mother Smokes / # of Cigs/Day
- Father Smokes / # of Cigs/Day
- Father Has Cough
- Family Income
- Father's Occupation
- Mother's Occupation
- Gas Cooking
- Child Shares Bedroom
- Family: # Cigs/Day
- Total Suspended Particulates
- Mass Median Diameter
- Coarse Fraction
- Fine Fraction

Table II. Respiratory Health Logistic Regression

Function: P = 1 / (1 + e * * -[A + B1X1 + B2X2 + ...])

SYMPTOM	COEFF	COEFF VALUE	VARIABLE	SIGNIF OF COEFF	CODE		
					Pres	,	Abs
Cough Day Or Night	A	-1.80	CONSTANT	(p<0.00001)	---		---
	B1	0.44	MACOF	(p<0.00001)	1	,	0
	B2	-0.34	HOSP<2yr	(p<0.001)	1	,	2
Episode of Cough And Phlegm >3 Weeks	A	-1.69	CONSTANT	(p<0.00001)	---	,	---
	B1	0.35	MACOF	(p<0.00001)	1	,	0
	B2	-0.29	HOSP<2yr	(p<0.001)	1	,	2
	B3	0.19	MASMOKE	(p<0.003)	1	,	0

Table III: Pulmonary Function Stepwise Multiple Linear Regression

Function: PULM. FUNC. = A + B1X1 + B2X2 + ...

PULMONARY FUNCTION VARIABLE	COEFF	COEFF VALUE	VARIABLE	SIGNIF OF COEFF	UNITS OR CODE	
					Pres ,	Abs
Height-Adjusted Peak Flow	A	4.220	CONSTANT	($p<0.00001$)	---	---
	B1	-0.010	FF	($p<0.00001$)	ug/m^3	
	B2	-0.049	SHAROOM	($p<0.04$)	1 ,	0
Height-Adjusted MEF 75	A	0.544	CONSTANT	($p<0.0001$)	---	---
	B1	0.125	MMD	($p=0.0001$)	um	
	B2	-0.002	MACIG	($p=0.0001$)	Cigs/Day	
	B3	0.067	HOSP<2yr	($p<0.02$)	1 ,	2

REFERENCES

1. Gschwandtner, G., and L. D. Pengelly. "Measurements of the frequency and location of stratified aerosol layers using a searchlight probing technique." Boundary Layer Meteorol. 14(3): 361-368, (1978).

2. Pengelly, L. D., and G. Gschwandtner. "Particulate pollution in the Nanticoke region," Report to Ontario Ministry of the Environment, and Ontario Hydro (1978).

3. "Operating Manual for Andersen 2000 Inc. High-Volume Particle Sizing Samplers," Andersen 2000 Inc., TR #76-900018, (1976).

4. A. Farhang. "Effect of wind on air quality in Hamilton, Ontario," Report AQRB - 83-001M, Environment Canada, Atmospheric Environment Service (1983).

5. Pengelly, L. D., A. T. Kerigan, C. H. Goldsmith and E. M. Inman. "The Hamilton study: Distribution of factors confounding the relationship between air quality and respiratory health," JAPCA 34:1039-1043, (1984).

6. Leeder, S. R., R. T. Corkhill, L. M. Irwig, W. W. Holland, and J. R. T. Colley. "Influence of family factors on the incidence of lower respiratory illness during the first year of life," Br. J. Prev. Soc. Med. 30:203-212 (1976).

7. Becklake, M. R., J. Soucie, G. W. Gibbs and H. Ghezzo. "Respiratory health status of children in three Quebec urban communities: An epidemiologic study," Bull. Eur. Physiopath. Respirat. 14:205-221 (1978).

8. Dockery, D. W., J. H. Ware, B. G. Ferris, Jr., F. E. Speizer, N. R. Cook and S. M. Kerman. "Change in pulmonary function in children associated with air pollution episodes," JAPCA 39:937-942(1982).

9. Florey, C.du V., R. J. W. Melia, S. Chinn, B. D. Goldstein, A. G. F. Brooks, H. H. John, E. B. Craighead and X. Webster. "The relation between respiratory illness in primary school children and the use of gas for cooking: III. Nitrogen dioxide, respiratory illness and lung infection," Int. J. Epidemiol 8:347-353 (1979).

10. Johnson, K. G., D. O. Loftsgaarden and R. A. Gideon. "The effects of Mount St. Helens volcanic ash on the pulmonary function of 120 elementary school children," Am. Rev. Resp.

Dis. 126: 1066-1069 (1982).

11. Kerrebijn, K. F., H. C. A. Hoogeveen-Schroot and M. C. Van Der Wal. "Chronic non-specific respiratory disease in children--A five year follow-up study," Acta Pediat. Scand. 261:7-72 (1977).

12. Love, G. J., S. P. Lan, C. M. Shy and W. B. Riggan. "Acute respiratory illness in families exposed to nitrogen dioxide ambient air pollution in Chattanooga, Tennessee," Arch. Environ. Hlth. 37:75-80 (1982).

13. Melia, R. J. W., C. du V. Florey and A. V. Swan. "Respiratory illness in British school children and atmospheric smoke and sulphur dioxide, 1973-1977: I. Cross-sectional findings," J. Epidemiol. Comm. Hlth. 35:161-167 (1981a)

14. Melia, R. J. W., C. Du V. Florey and S. Chinn. "Respiratory illness in British school children and atmospheric smoke and sulphur dioxide (1973-1977): II. Longitudinal findings," J. Epidemiol. Comm. Hlth. 35:168-173 (1981b).

15. Saric, M., M. Fugas and O. Hrustic. "Effects of urban air pollution on school-age children," Arch. Environ. Hlth. 36:101-108 (1980).

16. Speizer, F. E., B. Ferris, Jr., Y. M. M. Bishop and J. Spengler. Respiratory disease rates and pulmonary function in children associated with NO2 exposure," Am. Rev. Resp. Dis. 121:3-10 (1980).

17. Ferris, B. G. Jr., F. E. Speizer, J. D. Spengler, D. Dockery, Y. M. M. Bishop, M. Wolfson and C. Humble. "Effects of sulfur oxides and respirable particles on human health: Methodology and demography of populations in study", Am. Rev. Respirat. Disease 120:767-779 (1979).

18. Pengelly, L.D., A.T. Kerigan and S.R. Leeder. Discriminatory power of pulmonary function tests in children. Physiologist 23(4): Abstr. 387, 1980.

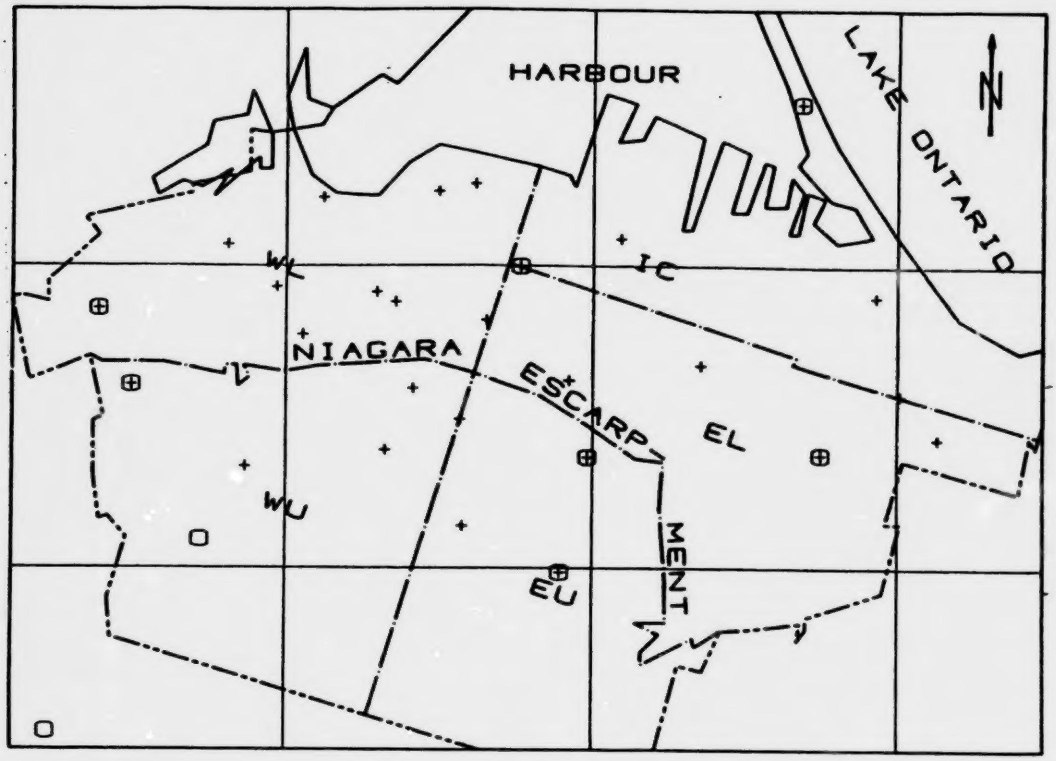
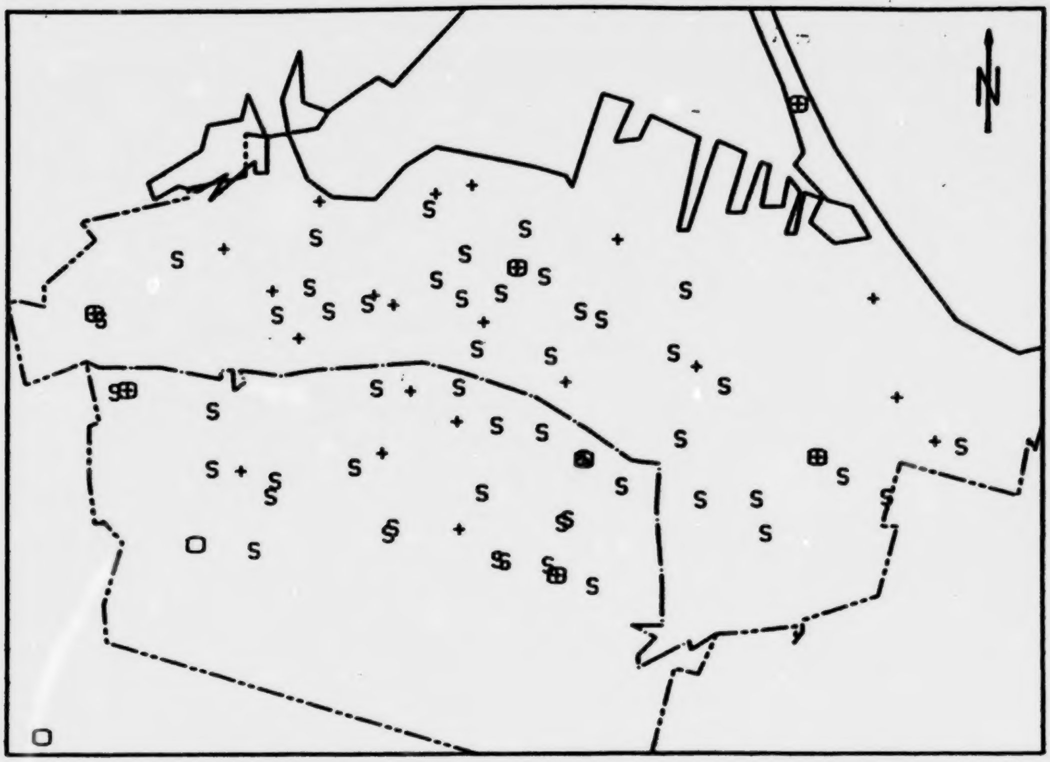


Figure 1 (A) Outline map of Hamilton, Ontario. City limits shown as broken line with two dashes; study area boundaries by broken line with dots. Grid lines are Universal Transverse Mercator at 5000 m intervals. Grid reference for the intersection point at "WL" is 590000 E, 4790000 N (Zone 17T). Crosses are TSP sites; open figures are PSD sites; a number of PSD sites are located at TSP sites.



(B) Same area as (A), but showing locations of schools ("S") as well as sampling sites

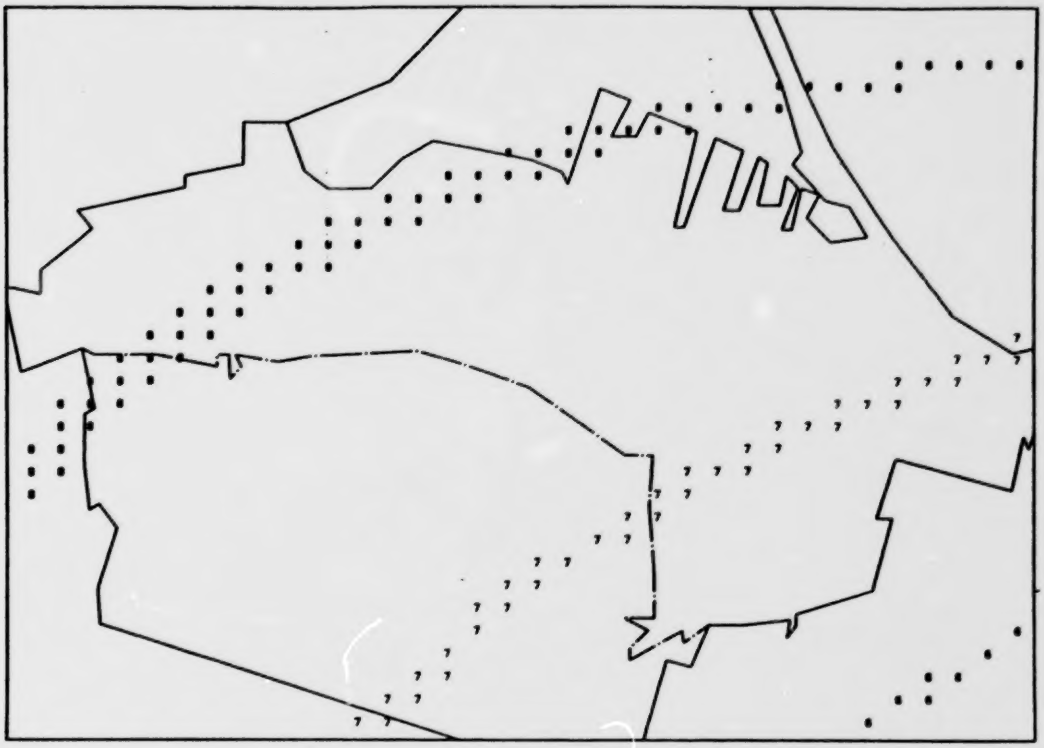
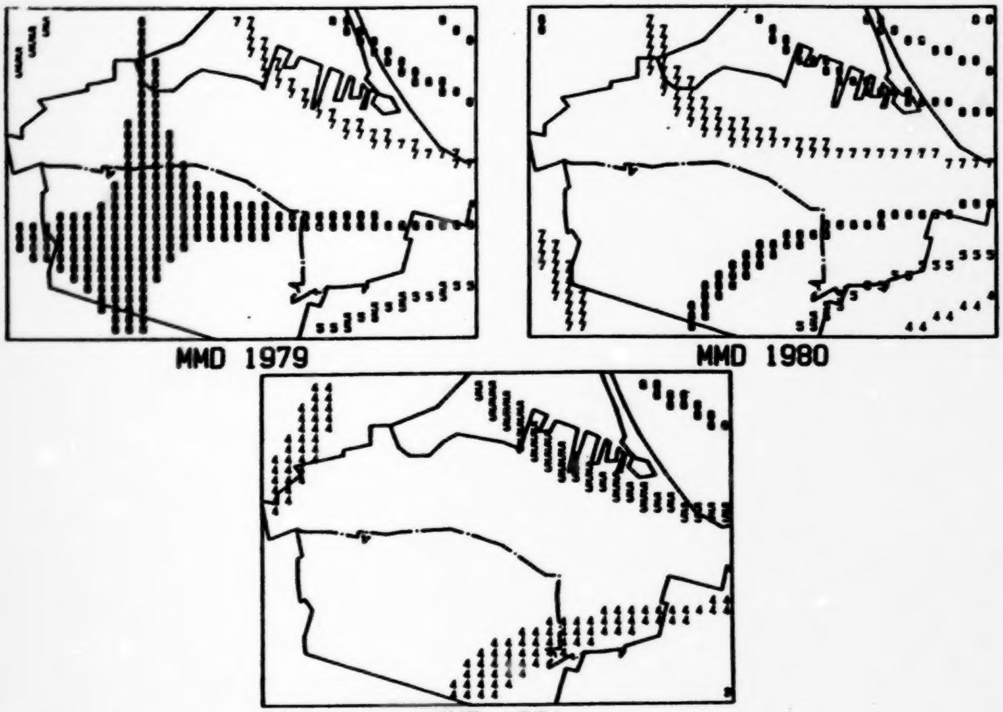


Figure 2 Distribution of particle size over the City of Hamilton for May, 1980. Contours of MMD derived from the response surface. Mass median diameter in micrometers may be obtained from the small numbers defining the isopleth by dividing by 2.

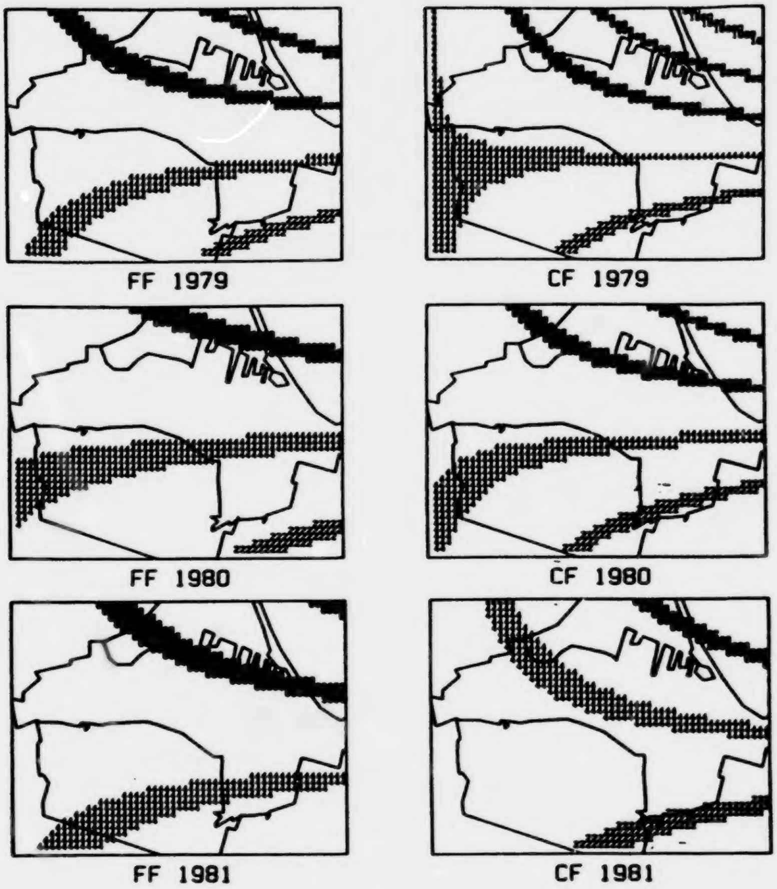


MMD 1979

MMD 1980

MMD 1981

Figure 3 Distribution of particle size over Hamilton: averages for three years. Contours derived from the response surface for yearly (12-month arithmetic mean) of MMD; isopleth system as in Figure 2.



FF 1979

CF 1979

FF 1980

CF 1980

FF 1981

CF 1981

Figure 4 Distribution of fine fraction: FF, (<3.3 um) and coarse fraction: CF, (>3.3 um) of particles over Hamilton for 3 years. Concentration defined by the isopleths in ug/m^3 are obtained by multiplying isopleth number by 10.

BIOLOGICAL MONITORING OF ENVIRONMENTAL GENOTOXICITY

M.L. Petras, J. Norsworthy, M. Vrzoc and K. Hill
Department of Biological Sciences
University of Windsor
Windsor, Ontario
N9B 3P4

Presented: Ontario Ministry of the Environment
Technology Transfer Conference
Toronto, Ontario

December 8, 1986

BIOLOGICAL MONITORING OF ENVIRONMENTAL GENOTOXICITY

M.L. Petras, J. Norsworthy, M. Vrzoc and K. Hill
Department of Biological Science, University of Windsor, Windsor, Ontario

Abstract

The SISTER CHROMATID EXCHANGE (SCE) assay has been modified so that wild mice can routinely be used to monitor the environment for general genotoxicity. The use of bromodeoxyuridine tablets and improvement of the staining procedure have permitted the processing of an adequate-sized sample (30 mice or more) at one time with consistently good results. This procedure has now been applied to wild mice collected from a number of localities in southwestern Ontario over the last three years. The annual temporal and geographic patterns have been similar from year to year. The SCE values/mouse are low in the early spring (prior to the spraying of crops with pesticides), high in the late spring (spraying period) and generally low in the summer (post-spraying period). The geographic pattern involves high SCE values in mice captured in the western part of the study area (Essex County) and lower values in those from the eastern section (Kent and Elgin Counties). Also we have examined the effects of a number of factors on SCE levels and their variability. These have included: short-term stress, age, genetic heterogeneity, some commonly used herbicides, several chemicals encountered in the plastics-molding industry and fumes in a diesel garage. Only chromic acid (plastics-molding industry) and diesel fumes significantly increased SCE values.

The MICRONUCLEUS ASSAY OF PERIPHERAL BLOOD was selected as a back-up system to permit corroboration of the SCE results. This assay was chosen because: 1) with fluorescence microscopy the typing of micronucleated cells is very straightforward and can be done rapidly, 2) the mouse is not sacrificed and blood samples from the same animal can be obtained at different times after treatment, 3) no pretreatment of animals is necessary prior to obtaining testable blood samples, and 4) a single recent (within 72 hours) exposure of an animal to a genotoxic agent can be distinguished from both an earlier exposure and chronic exposure. Furthermore, although most agents induce both SCEs and micronuclei there are some that cause the latter but not the former making the two tests complementary. So far a time-response curve has been developed for two compounds, cyclophosphamide and mitomycin C. Peak induction of micronuclei occurs at around 48 hours after injection of either agent. This appears to be about 12 hours later than induction of micronuclei in bone marrow cells. The micronucleus assay has been applied to wild mice being examined for SCEs as well as mice being used in several experimental situations.

The results of both tests will be presented, compared and discussed in detail.

(This research is supported by a grant from the Ontario Ministry of the Environment.)

BIOLOGICAL MONITORING OF ENVIRONMENTAL GENOTOXICITY

M.L. Petras, J. Norsworthy, M. Vrzoc and K.A. Hill
Department of Biological Sciences, University of Windsor, Windsor, Ontario

INTRODUCTION

Many of the studies being presented at this conference are concerned with the chemical and physical detection and analyses of pollutants. Such studies are essential, especially, since man has been extremely successful in saturating his environment with a plethora of agents which affect the quality of that environment and even his health. In considering the effects on man, we, however, frequently ignore the fact that the pollution problem is multifaceted, that many factors are interrelated and interwoven to give an end result and that physical measurement may not be relevant. It is, therefore, important that assessments of the effect of environmental pollution be done under biologically realistic conditions. This generally implies *in situ* monitoring. Although such monitoring may simply involve the measuring of toxic agents which have accumulated in organisms or the physiological effects of such agents in specific tissues, it is the short and long term genetic effects that generally are of most interest. Short term genetic damage may be reflected in the development of cancer or tumors, whereas the long term effects include the accumulation of deleterious gene mutations which are passed on from generation to generation.

In situ monitoring permits concentrating, under a set of natural conditions, on the effects of a single pollutant or occasionally a group of pollutants. It also permits general monitoring of the environment where the genotoxicants have not been specifically identified. In both situations a number of other factors enter the picture. These can be chemical, physical and even biological. Such factors may have either a promotional or an inhibitory effect on the agent(s) being monitored. In some instances, synergistic interaction may be encountered involving agents that alone, at best, would have very subtle effects. Furthermore, sometimes even nonmutagenic compounds may act synergistically with known mutagens.

Conversely, the use of laboratory strains of organisms, under laboratory conditions, could result in an overestimate of the genetic damage that is being caused by a certain agent or group of agents because wild (non-laboratory) organisms may tend to be more resistance to the agent(s) as a result of mutation and natural selection. Such resistance could, for example, be the result of the evolution of new detoxification steps, the lack of sensitivity to a particular agent, improved DNA repair efficiency.

In situ monitoring also provides data on temporal variations (seasonal, diurnal, biorhythmic) and geographic patterns. The latter may reflect the establishment of new industries, landfill sites, nuclear power plants, farming practices.

The SISTER CHROMATID EXCHANGE (SCE) TECHNIQUE in mice has been proposed as a sensitive, in situ monitoring system which can provide us with an EARLY WARNING ABOUT CHANGES IN GENOTOXIC LEVELS in the environment. The procedure which was described at this Conference several years ago has been modified so that it consistently gives good results with a minimum of technician effort. In the past eighteen months we have continued examining natural populations of the house mouse, Mus domesticus, for SCE levels in order to reinforce the 1983 and 1984 findings. In the process we have also developed a data set of currently "typical" SCE values against which future values may be compared. Such a data base should be especially valuable if and when the Detroit, Michigan incinerator comes on line or other pollution crises surface. Since seasonal fluctuations in SCEs have been observed and since we postulate these fluctuations to be associated with agricultural spraying, we have examined several herbicides that are commonly used in southwestern Ontario. In looking for a 'crisis' situation, that is one where genotoxic levels are high, we keyed on three industrial situations which we thought might be good candidates (a chrome-plating plant, a plastics processing shop and a diesel-repair garage). We have also been concerned about the reliability of the SCE technique when applied to wild mice. These include effects resulting from: a) stress encountered in trapping, transporting and general handling of the wild mice, b) the high genetic variability characteristic of wild mice, c) possible differences between inbred and wild mice in their response to mutagenic agents. We have also been concerned with improving the sensitivity of the SCE assay and to this effect we have been looking at several tumor/carcinoma/mutation promoting and inhibiting agents. Finally, we have spent considerable effort applying (and to a limited degree modifying) a second procedure, the ASSAYING OF MICRONUCLEI IN PERIPHERAL BLOOD of mice, so that we can substantiate the results of the SCE technique.

SCE ANALYSIS

In SCE studies, newly formed DNA strands are labelled with 5-bromo-2'-deoxyuridine (BrdU). This, after several chromosomal replications results in differential staining of two sister chromatids. Differential staining permits the detection of exchanges between such chromatids.

The introduction of BrdU was modified to permit the processing of a large number of mice within hours after being caught. This was done by switching from serial injections to implanting tablets. Each tablet was formed by compressing 50mg of BrdU. A tablet was then partly coated by melted paraffin, and inserted subcutaneously on the dorsum of anesthetized mice. Twenty-four hours later 4ug/g of colchicine were injected intraperitoneally and three hours after that the mice were sacrificed by cervical dislocation.

The rest of the procedure was also streamlined. Femurs were removed and bone marrow cells were flushed into a warm (37C) hypotonic KCl solution (0.075M). The cells then were put through two stages of fixation in a cold glacial acetic acid/methanol mixture. On fixation, the cell suspension was applied dropwise to slides and air dried. After a 24 hour aging period, the slides were incubated in a fluorescent stain, Hoechst 33258 (10ug/g of distilled water), for 15 minutes. The slides were then placed in a staining jar containing Sorensen's buffer (pH 8.0), covered with saran wrap and exposed to a bank of four fluorescent tubes at a distance of 15cm for approximately 23 hours. At the end of this period a single slide was removed and stained with Fisher's Giemsa for 8 minutes. If no differential staining was seen the rest of the slides were exposed to the fluorescent lights for another 10 minutes and another test slide was examined. This was repeated until satisfactory differential staining was observed and then all the remaining slides were stained.

The above procedure eliminates serial injections of BrdU and handling of slides individually until the scoring is to be done. It also permits the staining of large numbers of slides at one time, since test slides insure that no run is lost because of poor differential staining of the chromatids. This procedure is highly suitable for survey work because up to 30 mice can be sacrificed and processed relatively easily at one time. This permits the processing in a single run a large sample and an adequate-sized control group. Scoring can be done later.

CONTINUED MONITORING OF NATURAL MOUSE POPULATIONS FOR SCEs

The monitoring of natural populations of mice for sister chromatid exchanges begun in 1983 was continued into 1986. Again the mice were collected from corn cribs as they were being emptied. The SCE values of the mice collected in 1985 and 1986 are presented in Table 1. For comparison a summary of the 1985 and 1986 data are given together with those of the previous two years in Table 2.

In both 1985 and 1986 the Essex County samples showed seasonal peaks in June and July. This corresponds to the period when crops were being sprayed with herbicides. Unfortunately because no mice were obtained from Kent County during the prespraying season (farmers were not emptying cribs at this time) only Essex County samples can be examined for seasonal patterns. These patterns are consistent with those seen previously. The 1986 results from Kent County are unique, in this regard, because they show no seasonal patterns. Perhaps this is due to the small sample sizes obtained in May. Unlike the 1984 results, the sexes in the 1985 and 1986 samples differed significantly in SCE counts ($p < 0.001$). Females showed about 1.25 as many SCEs as males. This difference was consistent for nearly all samples and as a result both males and females showed similar temporal and geographic patterns. Differences between the two sexes have been found in other organisms. For instance, in lymphocyte cultures derived from humans exposed to ethylene oxide, cells derived from females had 8% more SCEs than those derived from males (see Evans, 1986).

Again as in earlier studies (Petras and Piscitalli, 1984), no correlation was observed between the SCE levels and the quantity of BrdU absorbed if the amount absorbed fell between 15 and 36mg/mouse. Ninety per cent of the mice examined were in this range.

During the spraying period the increases in SCEs generally ranged from 10% to 50%. The one major exception was the 1985 Trudell west sample; here the SCE level was 90% higher than the control. Evans(1986) comments that in many studies when small samples were exposed to mutagens, the increases of SCEs were often less than a factor of 2. For instance, smokers show between 16 and 30% more SCEs than non-smokers. So our results fall within these levels and suggest that although mutagenic agents are present in the environment the levels are such as to increase SCE levels only slightly. No persistent crisis situation has as yet been encountered.

POPULATION ENCLOSURES

Previous studies with outdoor population enclosures were short term; animals were placed in these containers for a month or less. These outdoor enclosurers are 90 litre galvanized garbage cans half filled with corn and covered with hardware cloth tops. The corn provides the mice with sufficient water, nutrients and protection. Animals are able to survive even midwinter conditions. These containers were placed at various sites in southwestern Ontario.

In 1984, mice had been placed in enclosures at four different sites: Renaud, Laramie, Rocheleau-McKim and Trudell. There appeared to be no geographic differences in SCE counts in these four regions in that year but there were seasonal differences. The SCE levels were higher in June than in any other period and they appear lowest in November.

In the past year we have begun a longer term experiment. Mice are being left in the enclosures four months instead of one or less. We are attempting to verify the patterns observed in 1985. This experiment was begun by putting mice in the containers August,1985, after the spraying season, and leaving them until mid-December. Three geographically distinct sites were used: Laramie (western Essex County) which gave counts and standard error of the mean of 4.14 and 0.18 per cell; McKim (central part of the county) which gave 2.97±0.36 SCEs per metaphase and Trudell (north-eastern region of the county) 4.28±0.28. The McKim values are the lowest observed in mice living under natural or seminatural conditions. This is not entirely unexpected for a winter sample with no recent herbicide contamination and from a site some distance from industrial population sources. The higher level of SCEs at Laramie's could be explained by the proximity of this site to several major industries. The high SCE values for the Trudell sample are unexpected unless they are affected by emission from the nearby small town of Tilbury. The Trudell farm is 35 miles east of Windsor. The enclosure values at Trudell's in 1985, are consistent with the SCE values of wild mice for that year. Both sets of values are high.

Studies on mice inhabiting population enclosures is continuing. One positive attribute of these animals is that they are inbred, therefore genetically identical and so genetic variance does not contribute to the differences between samples. The differences must then have an environmental basis. Similar differences observed between natural populations could then be primarily attributable to environmental factors.

Incidently, winter samples may be best to establish geographic patterns since there are no confounding factors such as the herbicides.

RELIABILITY OF SCE ESTIMATES IN WILD MICE

EFFECT OF STRESS ON SCEs IN MICE

Because animals after being caught are left in traps for several hours and are transported to the laboratory in these traps, the effect of stress on SCE's was considered. Some data on rats suggests that SCEs in these animals were in fact increased by stress.

Three-month old C3H mice were used in this experiment. They were divided into four treatment groups:

a) animals that were shaken hourly for a 15 minute duration on a mechanical shaker beginning four hours after BrdU implantation until the injection of colchicine 20 hours later.

b) animals that were forced to swim for a six minute period every two hours beginning four hours after BrdU implantation and ending with the injection of colchicine.

c) animals that were exposed to shaking for 15 minutes followed the next hour with swimming for 6 minutes. Again this treatment began four hours after BrdU implantation and continued with alternating shaking and swimming hourly until the injection of colchicine.

d) the control group that was composed of mice housed quietly in a cage nearby.

The SCE values in the treated animals did not differ significantly from those in the control group (Table 3), suggesting that exposure to limited stress had no significant effect on SCE levels. The combination of swimming and shaking should perhaps be studied further because it is in this group that the SCE levels were the highest.

The effect of car transportation on SCE levels in captured mice was also considered. On two occasions 3 C3H mice were placed in traps and transported by car to trapping sites and then back to the laboratory. None of the mice showed high SCE values. The mean (4.67 ± 0.87) did not differ significantly from the control group (4.45 ± 0.64).

There is, therefore, no indication that mild physical stress had an effect on SCE levels in inbred mice. As mentioned above the combination of swimming and shaking should be re-examined perhaps for a longer term. Also both of these experiments should be repeated using recently caught wild mice or at least laboratory-born descendents of wild mice. Finally, we should also stress the animals before BrdU implanting.

AGE AND SCE LEVELS

Mice collected from natural populations obviously vary in age. It is, therefore, essential to determine if there is correlation between SCE levels and age. Reimer and Singh (1983a) studying inbred strains C3H, C57BL/6J and Balb/c found a decline in SCEs induced by cyclophosphamide as the mice increased in age. However, no significant differences were observed in baseline SCEs of 11 and 33 week old mice. Differences due to age have been reported for human fibroblasts (Schneider and Gilman, 1979; Schneider et al, 1979). Age differences have also been seen in the number of micronucleated cells in cultures from donors of different ages. Approximately a four-fold increase has been observed in micronuclei in cultures from an 80-year-old donor when compared to a newborn donor (Fenech and Morley, 1985).

We have examined laboratory-born descendents of wild mice of various ages (Table 4) and found no correlation between age and noninduced SCE levels in mice. The mice were all adults with ages ranging from 2.5 to 9 months. These results are consistent with our earlier findings based on classifying wild mice into two categories: young (less than 15 g) and adult (more than 18 g). The SCE values were 6.28±0.21 for the former and 5.49±0.13 for the latter. This difference was not significant at the 5% level (t = -1.1749).

VARIANCES OF INDUCED SCE VALUES IN WILD AND INBRED MICE

The induction of SCEs is at least partly under genetic control. Reimer and Singh (1983b) found SCE induction to be controlled by polygenes. Several studies on human populations also indicate genetic control of SCE formation. For instance, there have been reports of differential induction of SCEs by mutagens in normal humans and individuals with xeroderma pigmentosa (Wolff et al, 1977; see also Wolff, 1984). King (1984) gives an overview of genetic susceptibility of humans to chemical exposures.

In natural populations of an organism, unlike the inbred strains, there is considerable genetic variability. The mouse populations of southwestern Ontario are no exception (Petras et al, 1979). This presents two questions about genetic variability. a) Does the level of SCE induction vary from one population to the next and from wild mice to inbred strains? b) Because of the genetic variability of natural populations as compared to inbreds is there a higher variance in SCE values in a sample of wild mice than in inbreds?

To answer both of these queries we compared SCE-induction by different concentrations of cyclophosphamide (CP) in an inbred strain and laboratory-born descendents of wild mice. Table 5 summarizes preliminary results of this experiment. The descendents of wild mice appear to be more susceptable to cyclophosphamide than do C3H mice for all three doses of CP tried. However, the variances of SCE frequencies from one dose to the next and between wild and inbred mice do not show heterogeneity. Bartlet's test of homogeneity of variances shows that the differences observed are not significant at the 5% level.

So although we found a difference in the means of the responses of wild and inbred mice, the variances of each of the groups were similar suggesting that the genetic heterogeneity of wild mice did not contribute to their variance and that the reliability of SCE measurements in wild mice was similar to that of inbreds. The differences in levels of response to SCE-inducing agents and the variability of response will continue to be examined.

ATTEMPTS TO FIND NATURAL (NON-EXPERIMENTAL) INDUCERS OF SCEs

THE EFFECT OF HERBICIDES ON SCE IN MICE

Since mice collected during the spraying season gave higher SCE values than those collected before or after, three herbicides widely used in southwestern Ontario were initially selected for a closer examination of their effects.

These were:

Lasso (alachlor; 2-chloro-2',6'-diethyl-N-(methoxymethyl)acetanilide) which is used as a preemergence treatment for corn and soybeans. It controls annual grasses.

Basogran (bentazon; 3-iso-propyl-2,1,3-benzothiadiazin-(4)-one-2, 2-dioxide) which is a postemergence herbicide recommended for control of various broadleaf weeds in peas, flax and in all beans and corn.

Kil-Mor is the trade name of a product composed of three herbicides: 2,4-D (2,4-dichlorophenoxyacetic acid), Mecoprop (d,1-2-(4-chloro-o-tolyloxy) -propionic acid) and Dicamba (3,6-dichloro-o-anisic acid. This mixture is used to control 'hard to kill' broadleaf and grasses in spring wheat, winter wheat, barley, flax, corn and oats.

The mutagenic activities of these herbicides have been evaluated to some extent. All have given negative results in the bacterial reversion-assay with five strains of Salmonella typhimurium and a strain of Escherichia coli (Moriya et al, 1983). Lasso has, however, been found tumorogenic in mice and 2,4-D has significantly increased SCE values in human lymphocytes exposed to 50ug/ml in the medium (Korte and Jalal, 1982). No information is available on possible syngergistic interactions of these agents.

Mice of the inbred strain, C3H, were injected intraperitoneally with either a pesticide dissolved in saline or just saline 12 hours after the implantation of BrdU tablets. The pesticide/saline injections were followed by colchicine injections 12 hours later and the mice were sacrificed 3 hours after the colchicine was given.

Preliminary studies showed that 300mg of Lasso/kg body weight injected intraperitoneally was a lethal dose whereas 150mg/kg was tolerated by the mice. As a result the mice were given 150, 75, 37.5 and 18.75mg/kg body weight. For

Basogran 600mg/kg was found to be lethal whereas 500mg/kg left one of four mice alive and 400 and 300mg/kg did not kill any mice. For Kil-Mor 291mg/kg body weight was toxic whereas 194 and 97mg/kg body weight were not.

The SCE results are given in Table 6. Although in all cases the highest dose of herbicide gave the highest SCE values, the differences between any herbicide-injected animals and saline-injected mice was not significant at the 5% level. If there is a relationship between SCE levels and these herbicides it is, at best, very subtle and would require a much larger sample size to establish. At present we must conclude that these herbicides are not responsible for the SCE shifts seen in natural populations of mice.

There are other herbicides and insecticides being used in the area. Several others Sevin, Chlordane and Diazinon are currently being tested and others will be in the future.

INDUSTRIAL SETTING AND SCE LEVELS

Three industrial sites were selected to see whether significant increases in SCE levels could be detected. A plastics-molding plant was included because such chemicals as polyvinyl chloride (Anderson et al, 1981), propylene oxide (Hogsted et al, 1983) and ethylene oxide (Hardin et al, 1983) associated with the plastics industry, have been found to be mutagenic and SCE inducers. Also a diesel-repair garage was chosen because the Ames Salmonella Test has revealed that such products of combustion as 9-nitroanthrocene and 1-nitropyrene caused marked induction of revertents (Pitts et al, 1982). Finally, a chrome-plating plant was picked because hexavalent chromium has caused gene mutations (Ohno et al, 1982; Bianch et al, 1983).

In each case six C3H male mice were placed in five gallon, plastic pails containing corn. The corn provided the mice with food, water and shelter. There was sufficient corn to maintain the animals for six weeks. The plastic containers housing the mice were placed in each of the work environments for two weeks. An identical container was kept as a control in the animal facility at the University of Windsor. Bone marrow cells were prepared for SCE analysis in the manner described earlier in this report.

The results are given in Table 7. The SCE counts in mice housed in the plastics-molding plant and the diesel garage showed modest but significant (5% level) deviations from the controls. These differences are not striking and as result the study should be repeated with a larger sample.

As a follow up to the in situ studies some of the more widely used chemicals, that is chemicals with which the workers came in contact in their daily activities were injected into C3H males two hours after the implantation of BrdU tablets. These included:

a) Waste Heat Transfer Oil - a highly stable oil that is used to heat molds used in production. This oil was diluted with an equal volume of corn oil.

b) Coolant - a chemical added to the water used in cutting steel in the process of building molds. This chemical was dissolve in an equal volume of 0.95% saline.

c) Chromic acid - an acid routinely used in a chrome plating plant.

The results are summarized in Table 8. The chromic acid more than doubled the SCE count. This was significant at the 1% level. The transfer oil increased the SCE level at about the 5% level of significance.

The chromic acid results are consistent with data in the literature.

Both the in situ exposure and the injection results suggest that in fact the SCE assay is sufficiently sensitive to uncover genotoxins in the industrial environment. However, the situations that we have uncovered in this study show only subtle increases in SCEs.

TREATMENT WITH RIVER WATER

In an effort to test the effectiveness of the SCE assay in monitoring genotoxicity of naturally occurring situations, water was obtained in September 1985 from two sources, the Detroit River (foot of the Ambassador Bridge) and Little River (one mile from its mouth). The Detroit River receives water from the upper Great Lakes including the St. Clair River. Little River is a small stream in the eastern section of Windsor, Ontario. It drains a number of industrial complexes including a chrome-plating plant and a fairly large agricultural area. This river is known as having a serious pollution problem. In the summer months there is frequently a heavy die-off of fish in this stream.

The mice were divided into two treatment groups and a control. Six animals were given five daily intraperitoneal injections of 10 ml/kg of raw water from either the Detroit River or Little River on consective days. The controls were injected with distilled water. The last injection was given 6 hours after the implantation of BrdU tablets. The same procedure was followed in a second run but this time all the water samples were concentrated five-fold by heating.

The results are summarized in Table 9. 'Raw' (unconcentrated) water from both rivers gave higher SCEs than the controls which were given distilled water. These differences are , however, not statistically significant. River waters concentrated by heating gave SCE values lower than that seen in their controls. A comparison of raw water and concentrated water from each source showed a siginificant difference for the Detroit River sample ($t=2.75$; d.f.=10; $p<0.05$). The difference between the two Little River samples was not significant. The difference in the latter case may be an underestimate because the control values for the heated water was 10% higher than for the unconcentrated water. Adjustment of the Little River 'postheating' values to compensate for the high control values would make the difference between the two Little River samples significant at the 6% level ($t=2.17$; d.f.=9). The difference between the SCEs induced by concentrated Detroit River water and its respective contol is significant ($t=2.56$; d.f.=10; $p < 0.05$). Unexpectedly these results indicated the Detroit River water to be less genotoxic than concentrated distilled water.

These experiments should be repeated with a larger sample size to determine if heating and concentrating the river waters has a real and persistent effect on the water's genotoxicity.

ENHANCEMENT OF SENSITIVITY OF SCE ASSAY

MUTAGEN INHIBITORS

Some preliminary experiments have been carried out with known inhibitors in an attempt to reduce the baseline count. If a reduction were seen this would be an indication that the mice in our animal facilities are exposed to genotoxic agents.

The inhibitors used were selenium (5.43mg/l) and ascorbic acid (25g/l). Both were dissolved together in drinking water and combined with sucrose (20/l). Sucrose was added to make the water more palatable. The mice were placed on this solution 16 days before BrdU was implanted. Six hours after the implantation cyclophosphamide (CP) (10mg/l) or saline were injected intraperitoneally.

No decrease in SCEs was observed in the baseline count (see Table 10) suggesting that either no inducing agent was acting on the baseline count or that the inducer(s) were not affected by the inhibitor. The inhibiting solution did affect the CP-induced SCE levels. The decrease was significant at the 1% level. Which of the two compound is responsible for the reduction remains to be determined.

MUTAGEN PROMOTORS

In an attempt to increase the sensitivity of the SCE assay we have also begun to examine some common mutation promotors.

Based on a survey of the literature we began to look at three compounds which have been commonly used in the past. These were arsenic (8mg/kg/injection), caffeine (80mg/kg/injection) and cyclamic acid (300mg/kg/injection). Each C3H mouse was given three injections at 8, 11, and 14 hours after BrdU implantation. The mutagen, if given, was given 7.5 hours after implantation.

Alone none of the three compounds increased the SCE count significantly over the baseline level (see Table 11). Cyclamic acid and arsenic appeared to inhibit CP induction of SCEs and caffeine appeared to have no effect. For mitomycin C , caffeine appeared to increase SCE induction slightly. The other two had no effect. Based on these results, we considered none of these compounds to be good candidates for increasing the sensitivity of the SCE assay.

A SECOND MONITORING SYSTEM

Several individuals have suggested the need for a second monitoring system to confirm the results of the SCE assays. Of the systems available we have examined the MICRONUCLEUS (MN) ASSAY FOR PERIPHERAL BLOOD. This assay has been described as less sensitive than the SCE assay by some (Bauknecht et al, 1977; Lasne et al, 1984) and equally sensitive by others (Cole et al, 1983). Furthermore it may be considered complementary to the SCE assay because SCE and MN inductions appear to be independent (Renault et al, 1982). Finally, the MN assay of peripheral blood is the backup procedure of choice because of properties (see below) which should prove valuable in studies of natural populations, in continuous monitoring of long term exposure effects and in genetic analyses. The selection of the MN assay was further enhanced by the acridine orange fluorescent staining technique describe by Hyashi et al (1983) and Tice (1985). This procedure appears to eliminate many of the scoring problems associated with Giemsa. As a result, we have begun to develop a time-response profile for several genotoxins to determine optimal bleeding times and we have also begun to determine the frequencies of micronucleated erythrocytes of wild mice and treated inbred animals for comparison with SCE data.

MICRONUCLEUS ASSAY-CHARACTERISTICS

Heddle (1973) has described the micronucleus assay as simpler, faster and easier to score than other cytological monitors of genotoxicity (see also: Salamone and Heddle, 1983). Generally micronuclei are formed as fragments of chromosomes which have lost their centrioles and therefore lag behind in the cytoplasm when the nucleus is reformed. A second, perhaps less common process, involves the detachment of a whole chromosome from the spindle apparatus. This second mechanism may be increased through the use of spindle poisons (Schmid, 1975).

Usually micronuclei have been assayed in polychromatic cells (PCEs) of bone marrow. These cells occur as the penultimate stage in erythrocyte formation. Tice and Ivett (1985) have summarized the positive features of the bone marrow micronucleus assay. The advantages include: a) micronuclei can be identified quickly in anucleated polychromatic erythrocytes, b) metaphase preparations are not required since interphase cells are used, c) newly formed cells reside in bone marrow only about 24 hours, therefore, any increase in micronucleated polychromatic cells is an indication of a recent exposure to a mutagen and d) there is a strong correlation between cancer-induction and micronucleus induction. The drawbacks of the bone marrow assay include DNA-nonrelated causes of micronuclei and the inability to do sequential sampling since animals are killed to assay bone marrow material.

To overcome the last problem MacGregor et al (1980) suggested assaying for micronuclei in polychromatic (PCEs) and normochromatic erythrocytes (NCEs) of peripheral blood since sacrificing of mice is not required. Furthermore, since PCEs are converted, within 72 hours after their formation in bone marrow, to NCEs, the time when exposure occurred can be divided into two periods, a recent 72 hours period and an earlier 35-50 day period since PCEs have a life span of up to 48 hours in peripheral blood and NCEs have a life span of 35-50 days. Unlike the situation in rats and humans, the cells with micronuclei are not preferentially removed from peripheral blood of mice (MacGregor et al, 1980; Schlegal and MacGregor, 1982). This permits distinction between a single recent exposure to a mutagenic agent and chronic exposure.

GENERAL PROCEDURE

The basic procedure used was obtained from R.R. Tice (personal communication). The following steps are involved: a) peripheral blood is obtained from a mouse by inserting a heparinized tube into the suborbital sinus; b) a drop of blood is spread evenly on the microscope slide; c) the slide is air dried and fixed in absolute methanol for 15 minutes; d) after 24 hours of aging the slide is stained with acridine orange (0.06125mg/ml of pH 7.4 phosphate buffer) for 3 to 4 minutes, then rinsed in buffer and washed in buffer for 6 minutes; e) the spread is covered carefully, to avoid air bubbles, with a cover slip; f) the slide is then examined under fluorescence microscopy (FITC filter combination, excitation wavelength 495nm, emission wavelength 520nm) and scored for i) number of micronucleated NCEs in 1000 NCEs, ii) number of micronucleated

PCEs in 1000 PCEs, and iii) percentage of PCEs in 1000 erythrocytes.

Under fluorescence, micronuclei which have been stained with acridine orange appear green, NCEs brownish-green and PCEs reddish-orange. If either the fluorescence or background stains are not suitable, the slide can be destained with absolute methanol and restained.

Acridine orange [494-38-2] discriminates between DNA which fluoresces green and RNA which fluoresces red. Acridine orange also binds to acid polysaccharides resulting in bright red fluorescence. These properties make the scoring of micronuclei relatively straightforward (Hayashi et al, 1983).

TIME RESPONSE STUDY FOR OPTIMAL RESULTS

After obtaining consistently good slide preparations so that scoring micronucleated PCEs and NCEs presented no difficulties, a profile of time-dependent induction of micronuclei was developed for two compounds, Cyclophosphamide (CP) and Mitomycin C (MMC). Other compounds, including methylmethanesulfonate, benzene, 6-mercaptopurine, and 7,12 dimethylbenzantracene, are either being or will be examined. These compounds have been chosen because they have been found to show different time responses in inducing bone marrow micronucleated PCEs (Hayashi et al, 1984; Salamone et al, 1980).

CP (50mg/kg), MMC (2mg/kg) or saline were injected once,intraperitoneally, into four, five month old C3H male mice. Blood samples were taken from the suborbital sinuses. The first samples were taken just before injection and then at regular intervals (see Figure 1). The last blood samples were taken 23 days after the first to see if the micronucleated cells returned to the starting level.

For both CP and MMC the maximum effect on PCEs was reached around the 48 hour period (Figure 1). This is about 24 hours later than in bone marrow cells for the MMC treated mice (Hayashi, 1984) and 12 hours later for CP treated animals (MacGregor et al, 1980). The increase of micronucleated cells was detected in the NCEs between 24 and 48 hours later. This increase of micronuclei in NCEs was not as dramatic as in the PCEs because of the dilution of micronucleated cells. Since NCEs last 35-50 days, the effect of a single injection is diluted about ten-fold. Calculations based on the micronucleated PCEs observed would suggest that from a single injection, at the concentrations used, the maximum micronucleated NCE count should be about 3 (Hayashi et al, 1984).

Another set of data collected was the percent of PCEs observed in the various samples. In the controls the percent of PCEs increased with each bleeding except for the last (552 hrs). This is not unexpected since the production of erythrocytes was stimulated by the removal of blood. In mice injected with CP the same pattern was observed but the production of new PCEs was reduced by almost 50%. MMC appeared to inhibit almost completely the production of new PCEs. By the 23rd day the PCE levels were almost back to the pretreatment values.

This phase of the study suggests that mice should be examined about 48 hours after their exposure to a mutagen and that in the first 24 hours although there is an effect on the frequency of micronucleated PCEs that effect is not nearly as strong as the 48 hour effect.

Wild mice should be examined for micronuclei in peripheral blood PCEs within 48 hours of being trapped. If the exposure to a genotoxic agent was short-term, that is a single pulse, then the micronucleated NCEs should be low, with a peak being reached 24 to 48 hours after the PCE maximum. If the exposure is chronic then the frequency of micronucleated NCEs should be much higher and should persist at a higher level (see Schlegal and MacGregor, 1982; Salamone and Heddle, 1983).

The percent of PCEs in peripheral blood may also be an indicator of agents in the environment which inhibit cell replication in the bone marrow. Just how meaningful this parameter may be, has yet to be determined.

MICRONUCLEI AND NATURAL POPULATIONS

Table 12 summarizes the MN values observed in the wild mice collected in 1986. Very little variability was observed. No geographic or temporal patterns are evident. This suggests that the MN assay may be less sensitive than the SCE analyses.

MALATHION, BENZENE AND MICRONUCLEI

Preliminary micronucleus-induction information has been obtained for several other compounds including malathion and benzene. Malathion was examined because it is commonly used to control ectoparasites in laboratory animals and we were concerned about the effect that occasional dunking of mice had on the frequency of micronucleated cells. Malathion has been described as genotoxic when injected. Our experiment involved topical exposure by dunking the mice in a 5% solution of commercially available (Purina) malathion. Malathion did not appear to increase the frequency of micronucleated cells (Table 13).

Benzene was examined as a prelude to developing a 'crisis situation' for SCE studies. Mice were exposed to benzene vapor by placing 0.25ml in the bedding hourly for 6 hours. The mice were examined for micronucleated PCEs and NCEs 48 hours after the last 'treatment'. A 3-fold increase was seen in the micronucleated PCEs (Table 13). These results are consistent with the findings of others.

EFFECT OF STRESS ON MICRONUCLEI

The same mice used in the SCE assay for the effect of stress (see above) were bled and also assayed for micronuclei. The results summarized in Table 14 appear consistent with the SCE data. The deviations from the control values were not significant.

INDUSTRIAL SETTINGS AND MICRONUCLEI

The mice that had been placed in the chrome plating plant were also assayed for micronucleated NCEs and PCEs in peripheral blood. See Table 15. These are consistent with the results obtained for the SCE assay (Table 7).

OCTACHLOROSTYRENE AND RIVER WATER

Octachlorostyrene (OCS) is a byproduct of industrial processes involving carbon and chlorine reactions at high temperature which has found its way into the Great Lakes and has been isolated from fishes (Kuehl et al, 1976) and from herons (Reichel et al, 1977). Both in short-term and long-term studies Chu et al (1984,1986) described this compound as having a serious effect on hepatic microsomal enzymes, serum components, the kidney and the thyroid gland at, in some cases, concentrations as low as 5ppm in rats. Also accumulation of OCS has been found in adipose tissue. No information is available on the genotoxicity of this compound, although Chu et al (1986), in their long-term study, report no induction of tumors attributable to OCS.

Since this compound is found in the Detroit River and was available to us in highly purified form we decided to see what effect it had on micronucleus induction. In our study we injected intraperitoneally into C3H male mice 200, 400 and 800mg/kg of OCS (obtained through Dr. P. Hebert from the Great Lakes

Institute, University of Windsor). The mice were bled at 24 hour intervals beginning just prior to the injection of OCS. The results of the 800mg/kg dose are presented in Table 16. Since the frequency of micronucleated cells at various times after the injection of this dose of OCS does not differ from the frequency prior to the injection, no attempt was made to score animals receiving lower doses.

These findings suggest that octachlorostyrene is not an inducer of micronuclei in mice and therefore probably not mutagenic.

SUMMARY

1] The SISTER CHROMATID EXCHANGE (SCE) ASSAY is now being used routinely in monitoring wild mice and mice exposed to various treatments or conditions.

2] Monitoring natural populations of the house mouse is continuing. A data base on SCE levels in popultions of various parts of southwestern Ontario is being developed. Both geographic and seasonal patterns have been observed over a four-period. Similar patterns are also being observed in inbred mice placed in population enclosures.

3] The reliability of the SCE values of wild mice to monitor the environment is being examined by studying the effects of stress, age and genetic variability on SCE. All of these indicate that the SCE assay on wild mice is a suitable test for monitoring environmental genotoxicity levels.

4] Various situations have been and are being examined to further test the suitability of the SCE in mice for monitoring the environment for genotoxin levels. These include herbicide-spraying practices, industrial settings and aquatic environments. Increases in SCEs have been seen in a number of cases but even when significant the increases have been modest.

5] In an effort to increase the sensitivity of the SCE assay we have begun to examine known inhibitors and promotors of mutagens/carcinogens for their effects. Of the battery of chemicals available which are known to promote genotoxic activity, the few examined so far appear to have only subtle effects.

6] As a backup or complementary system the MICRONUCLEUS ASSAY OF PERIPHERAL BLOOD appears to be a good candidate. This test appears to be quite sensitive for detecting certain genotoxic agents and has the advantage of being applied serially since the animals are not sacrificed. We are now applying this assay to most of the mice being tested for SCEs.

7] A time-response study has been done on two compounds, cyclophosphamide and mitomycin C, using the Peripheral Blood Micronucleus Assay. Peak effects in terms of the frequency of micronucleated polychromatic erythrocytes (PCEs) are reached 12 to 24 hours after similar peaks are observed in bone marrow tissue.

8] The Peripheral Blood Micronucleus Assay has also been applied to several experimental situations, in some cases as a followup to the SCE work while in others, preceding SCE studies. Malathion, octachlorostyrene and some of the industrial exposures had no effect on the frequency of micronucleated PCEs while benzene did.

CONCLUSIONS

The work is progressing well in a number of different areas. The SISTER CHROMATID EXCHANGE ASSAY is now pratical for samples of 30 animals and gives consistent results. The PERIPHERAL BLOOD MICRONUCLEUS ASSAY with acridine orange as the stain should serve as an excellent complement to the SCE test.

REFERENCES

T. Baucknecht, W. Vogel, U. Bayer and D. Wild. 1977. Comparative in vivo mutagenicity testing for SCE and micronucleus induction in mouse bone marrow. Hum. Genet. 35:299-307.

M.A. Bender, H.G. Griggs and J.S. Bedford. 1974. Mechanisms of chromosomal aberration production. III. Chemical and ionizing radiation. Mutat. Res. 23: 197-201

I. Chu, D.C. Villeneue, V.E. Secours, A. Yagminas, B. Reed and V.E. Valli. 1984. Octachlorostyrene: A 90 day toxicity study in the rat. Fundam. Appl. Tox. 4: 547-557.

I. Chu, D.C. Villeneue, V.E. Secours, V.E. Valli, S. Leeson and S.Y. Shen. 1986. Long term toxicity of octachlorostyrene in the rat. Fundam. Appl. Tox. 6: 69-77.

R.J. Cole, J. Cole, L. Henderson, N.A. Taylor, C.F. Arlett and T. Regan. 1983 Short term tests for transplacentally active carcinogens, II. A comparison of the sister-chromatid exchange and the micronucleus test in mouse foetal liver erythroblasts. Mutat. Res. 113: 61-75.

J.T. Evans. 1986. What has been achieved with cytogenetic monitoring? In Monitoring of Occupational Genotoxicants, ed. M. Sorsa and H. Norppa. Liss, New York.

M. Fenech and A.A. Morley. 1985. The effect of donor age on spontaneous and induced micronuclei. Mutat. Res. 148: 99-105.

M. Hayashi, T. Sofuni and M. Ishidati. 1983. An application of acridine orange fluorescent staining to the micronucleus test. Mutat. Res. 120: 241-247.

M. Hayashi, T. Sofuni and M. Ishidati. 1984. Kinetics of micronucleus formation in relation to chromosomal aberrations in mouse bone marrow. Mutat. Res. 127: 129-137.

J.A. Heddle. 1973. A rapid in vivo test for chromosome damage. Mutat. Res. 18: 191-197.

H. Kato. 1973. Induction of sister chromatid exchanges by UV light and its inhibition by caffeine. Exp. Cell. Res. 82: 383-390.

M.C. King. 1984. Genetic and epidemologic approaches to detecting genetic susceptibility to chemical exposures. In "Banbury Report" 16: 377-392, G.S. Omenn and H.V. Gelboin (ed). Cold Spring Harbor Laboratory.

C. Korte and A.M. Jalal. 1982. 2,4-D induced clastogenecity and elevated rates of sister chromatid exchanges in cultured human lymphocytes. Jour. Heredity 73: 224-226.

D.W. Kuehl, H.L. Kopperman, G.D. Veith and G.E. Glass. 1976. Isolation and identification of polychlorinated styrenes in Great Lakes fish. Bull. Environ.

Contam. Toxicol. 16: 127-132.

C. Lasne, Z.W. Gu, W. Venegas and I. Chouroulinkov. 1984. The in vivo micronucleus assay for detection of cytogenetic effects induced by mutagen-carcinogens: comparison with in vitro sister-chromatid exchange assay. Mutat. Res. 130: 273-282.

J.T. MacGregor, C.M. Wehr and D.H. Gould. 1980. Clastogen-induced micronuclei in peripheral blood erythrocytes: the basis of an improved micronucleus test. Environ. Mutatagen. 2:509-514.

M. Moriya, T. Ohta, K. Watanabe, T. Miyazawa, K. Kato and Y. Shirasu. 1983. Further mutagenicity studies on pesticides in bacterial reversion assay systems. Mutat. Res. 116: 185-216.

M.L. Petras and R. Piscitelli. 1984. Monitoring genotoxicity in the environment using sister chromatid exchanges in mice. Technology Transfer Conference Proceedings (Ontario Ministry of the Environment) 5: 717-740.

M.L. Petras, J.D. Reimer, F.G. Biddle, J.E. Martin and R.S. Linton. 1969. Studies of natural populations of Mus. V. A survey of nine loci for polymorphisms. Can. J. Genetics and Cytol. 11: 497-513.

D.L. Reimer and S.M. Singh. 1983a. Cyclophosphamide-induced in vivo sister chromatid exchanges (SCE) in Mus musculus. II. Effect of age and genotype on SCE, micronuclei and metaphase index. Mech. Aging Dev. 9: 303-311.

D.L. Reimer and S.M. Singh. 1983b. Cyclophosphamide-induced in vivo sister chromatid exchanges (SCE) in Mus musculus. III. Quantitative genetic analysis. Genetics 105: 169.179.

G. Renault, A. Gentil and I. Chouroulinka. 1982. Kinetics of induction of sister chromatid exchanges by X-rays through two cell cycles. Mutat. Res. 94: 359-368.

W.L. Reschel, R.M. Prouty and M.L. Gay. 1977. Identification of polychlorinated styrene compounds in heron tissue by gas-liquid chromatography-mass spectrometry. J. Assoc. Off. Anal. Chem. 60: 60-62.

M.F. Salamone and J.A. Heddle. 1983. The bone marrow micronucleus assay: rationale for revised protocol. In Chemical Mutagens: Principles and Methods For Their Detection (ed. de Serres). vol. 8: 111-149. Plenum, New York.

M. Salamone, J. Heddle, E Stuart and M. Katz. 1980. Towards an improved micronucleus test: Studies on 3 model agents, mitomycin C, cyclophosphamide and dimethylbenzanthracene. Mutat. Res. 74: 347-356.

R. Schlegal and J.T. MacGregor. 1982. The persistence of micronuclei in peripheral blood erythrocytes: Detection of chronic breakage in mice. Mutat. Res. 104: 367-369.

W. Schmid. 1975. The micronucleus test. Mutat. Res. 31: 9-15.

E.L. Schneider and B. Gilman. 1979. Sister chromatid exchange and aging. III.

The effect of donor age on mutagen-induced sister chromatid exchange in human diploid fibroblasts. Hum. Genet. 46: 57-63.

E.L. Schneider, D. Kram. Y. Nakanishi, B. Monticone, R.R. Tice, B.A. Gilman and M.L. Neider. 1979. The effect of aging on sister chromatid exchange. Mech. Aging Dev. 9:303-311.

D.G. Stetka, Jr. 1982. Operative and non-operative mechanisms of sister chromatid exchanges. In Sister Chromatid Exchange ed. A.A. Sandberg. Liss, New York.

R.R. Tice and J.L. Ivett. 1985. Cytogenetic analysis of bone marrow damage. In Toxicology of the Blood. R.D. Irons (ed). Raven Press.

S. Wolff. 1984. Use of sister chromatid exchanges (SCEs) to determine possible genetic predisposition in the response to chemical exposure. In "Banbury Report" 16: 333-341, G.S Omenn and H.V. Gelboin (ed). Cold Spring Harbor Laboratory.

S. Wolff, B. Rodin and J.E. Cleaver. 1977. Sister chromatid exchanges induced by mutagenic carcinogens in normal and xeroderma pigmentosum cells. Nature 265:347-349.
0

Figure 1: The effect of cyclophosphamide and mitomycin C on micronucleated a) polychromatic erythrocytes (PCE), b) normochromatic erythrocytes (NCE) in peripheral blood, and c) the production of new PCEs.

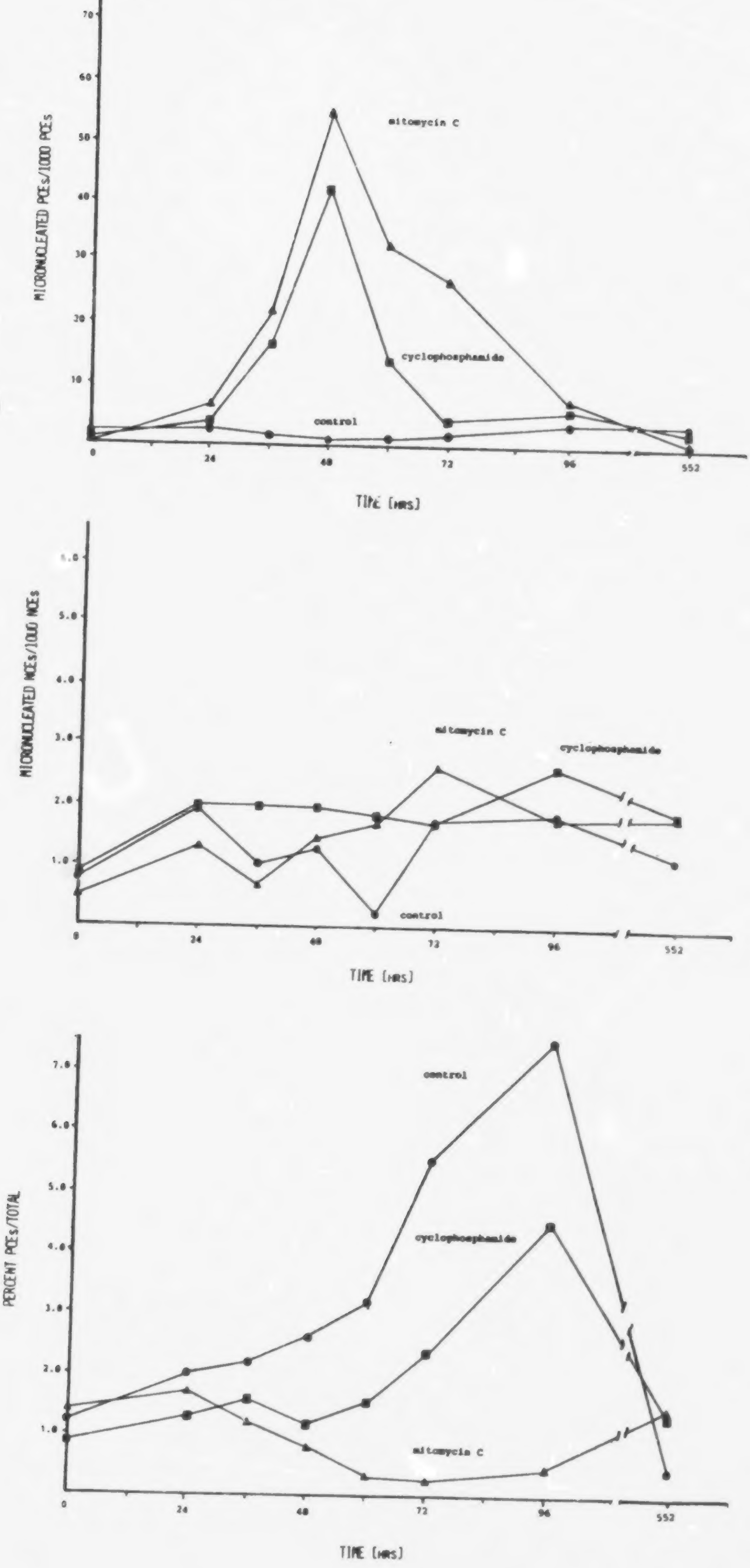


TABLE 1a. SCE levels in wild mice collected from corn cribs in three regions of southwestern Ontario before, during and after the spraying of crops with herbicides during 1986. Since there was a significant differences between the sexes, the sexes are considered separately.

LOCALITY	DATE	SCE COUNTS + S.D.					
		PRESPRAYING		SPRAYING		POST-SPRAYING	
		FEMALES	MALES	FEMALES	MALES	FEMALES	MALES
ESSEX COUNTY: (86)							
McKim	4/18	5.35(6) ±1.06	4.18(4) ±0.50				
Renaud	5/26	4.84(5) ±0.50	4.15(5) ±0.38				
Amlin	6/04			6.72(10) ±1.39	6.24(6) ±0.97		
Goulin	6/10			8.46(6) ±1.00	6.69(6) ±1.02		
Holden	6/11			7.18(3) ±0.75	5.38(3) ±0.66		
Farrough	8/04					5.75(10) ±1.41	5.81(9) ±0.69
Boide	9/04					7.00(7) ±1.57	5.70(6) ±0.61
Total		5.12 ±0.86	4.16 ±0.41	7.34 ±1.40	6.19 ±1.01	6.26 ±1.23	5.76 ±0.52
KENT COUNTY: (44)							
Dilliot	5/08	5.98(2) ±0.11	5.28(2) ±0.46				
Lucio	5/21	6.20(5) ±1.36	5.21(5) ±1.13				
Sheldon	5/14		5.22(2) ±0.32				
Oskar	6/23			5.30(7) ±0.78	4.85(4) ±0.47		
Cl'dening W	7/08			6.63(2) ±1.17	5.67(7) ±1.41		
Bokor	7/08			7.43(4) ±1.39	6.35(4) ±1.66		
Total		6.14 ±1.11	5.23 ±0.82	6.09 ±1.35	5.63 ±1.34		

Number in parenthesis is the size of the sample.

TABLE 1b. SCE levels in wild mice collected from corn cribs in three regions of southwestern Ontario before, during and after the spraying of crops with herbicides during 1985. Since there was a significant differences between the sexes, the sexes are considered separately.

		SCE COUNTS + S.D.					
LOCALITY	DATE	PRESPRAYING		SPRAYING		POST-SPRAYING	
		FEMALES	MALES	FEMALES	MALES	FEMALES	MALES
ESSEX COUNTY:							
McKim	5/11	5.48(4) ±0.46	5.41(4) ±0.21				
Borrowman	5/20	6.30(3) ±0.42	4.71(4) ±0.73				
Rocheleau	5/16		4.53(5) ±0.33				
Goolan	5/23	5.21(6) ±0.36	4.65(4) ±0.27				
Renaud	6/8			5.52(2) ±0.03	5.45(2) ±0.60		
Wright	6/8			6.52(3) ±0.78	6.05(1)		
Trudell	5/31			9.03(4) ±1.81	6.53(4) ±0.65		
Trudell E.	7/22			9.22(3) ±1.06	4.99(4) ±1.52		
Pook	7/31					11.00(2) ±2.50	
Boide	8/27					7.40(3) ±0.83	5.23(5) ±0.60
Total		5.54(13) ±0.25	4.93(17) ±0.33	7.92(12) ±0.74	5.70(11) ±0.59	8.84(5) ±1.24	5.58(5) ±0.53
KENT COUNTY:							
Allen	6/11			6.13(7) ±0.54	5.55(5) ±0.47		
McKinley	6/17			7.20(2) ±0.15	5.95(4) ±0.36		
Oskar	6/17			6.85(3) ±0.43	5.92(5) ±0.18		
Clenndening	6/18			7.00(2) ±0.60	5.23(4) ±0.45		
Cl'dening W	6/26			5.90(2) ±0.05	4.53(3) ±0.20		
Total				6.34(16) ±0.25	5.51(21) ±0.18		
ELGIN COUNTY:							
Brown	7/3			4.81(4) ±0.47	4.68(3) ±0.48		

Number in parenthesis is the size of the sample.

TABLE 2. SCE levels in wild mice collected from corn cribs in three regions of southwestern Ontario before, during and after the spraying of crops with herbicides over a four year period. Mice collected in 1984, 1985 and 1986 had 50 mg BrdU tablets implanted for SCE staining whereas the 1983 were injected with 80 mg of BrdU.

YEAAR	LOCALITY	SCE COUNTS + S.E.M.		
		PRESPRAYING	SPRAYING	POST-SPRAYING
1986	Essex County	4.64±0.22 (20)	6.76±0.16 (34)	6.01±0.24 (32)
	Kent County	5.69±0.41 (27)	5.86±0.38 (17)	
1985	Essex County	5.16±0.16 (30)	7.07±0.43 (24)	7.21±0.84 (10)
	Kent County		5.92±0.36 (37)	
	Elgin County		4.74±0.31 (7)	
1984	Essex County	5.70±0.19 (28)	6.35±0.17 (32)	
	Kent County	4.65±0.43 (19)	6.66±0.24 (38)	4.89±0.18 (30)
	Elgin County		6.62±0.46 (20)	
1983	Pooled data	5.99±0.32 (12)	9.22±0.86 (10)	

The numbers in parentheses are the sample sizes.

Table 3. Effect of Stress on Sister Chromatid Exchange in C3H males

Treatment	Number of Mice	SCE ± SEM
Control	4	4.28 ± 0.30
Swimming only	3	4.78 ± 0.54
Shaking only	3	4.40 ± 0.28
Swimming and Shaking	3	5.55 ± 0.49

Table 4 Correlation between age and SCE levels in laboratory-born descendents of wild mice.

	Laboratory born descendents of Wild mice		
Source	Age	Number of Mice	SCE Values ± SEM
Houle	2 1/2 months	6	6.2099 ± 0.54
Borrowman E.	3 months	3	6.6333 ± 0.62
Houle	4 months	6	6.4083 ± 0.49
Houle	5 months	6	4.8021 ± 0.44
Paquette	7 months	6	5.0250 ± 0.17
Paquette	9 months	6	6.1167 ± 0.54

There is no significant correlation between age and SCE values.

Table 5. Variances of SCE values in wild and C3H mice given varying amounts of cyclosphosphamide.

Mice	CP Level	Number of Mice	SCE	Variance
Wild Offspring	0.00	4	6.1625	1.9293
	0.045	11	5.350	0.9149
	0.45	4	7.8750	3.5608
	4.5	9	18.0777	4.7961
C3H	0.00	4	4.1825	1.4938
	0.045	4	4.3375	0.4255
	0.45	5	6.2500	0.4662
	4.5	4	12.6125	6.5485

Bartlet's test of homogeneity of variances shows that the differences are not significant.

TABLE 6: Mean SCE values in C3HeB/FeJ male mice receiving intraperitoneal injections of herbicides dissolved in saline or just saline.

TREATMENT (mg/kg body weight)		NO. OF MICE	MEAN SCE/CELL ± SEM	
Saline		15	4.96	0.33
Lasso	150	4	6.01	0.51
	75	4	4.23	0.12
	37.5	4	4.58	0.17
	18.75	4	5.31	0.54
Basogran	500	1#	5.90	
	400	4	4.51	0.25
	300	4	5.06	0.52
Kil-Mor	194	4	5.40	0.21
	97	4	4.32	0.34

# Only one of four survived the treatment.

TABLE 7: Mean SCE values in C3H male mice placed in cages partially filled with corn in three different industrial settings.

SITE	NO. OF MICE	MEAN SCE/CELL ± SEM	
University (controls)	6	4.61	0.04
Plastics-molding plant	5	5.63	0.27*
Diesel garage	6	7.05	0.53*
Chrome plating plant	7	5.47	0.02

* Deviation from controls significant at the 5% level.

TABLE 8: Mean SCE values in C3H male mice injected with three common chemical found in the industrial settings studied.

CHEMICAL	NO. OF MICE	DOSE	MEAN SCE/CELL ± SEM	
Transfer oil	3	3.75 ml/kg	6.05	1.15*
Coolant	3	3.75 ml/kg	5.67	1.48
Chromic acid	3	15 mg/kg	9.05	0.80**
Control	3		4.43	0.19

* Deviation from controls significant at the 5% level.
** Deviation from controls significant at the 1% level.

TABLE 9: Mean SCE values in C3H male mice receiving five daily injections of water obtained from the Detroit River and Little River, a small stream that drains several industrial complexes including a chrome plating factory. The water from the rivers and the distilled water injected into the controls was either raw (unconcentrated) or concentrated five-fold by heating.

TREATMENT	NO. OF MICE	MEAN SCE/CELL ± SEM	
UNCONCENTRATED WATER (raw):			
Controls	5	5.12	0.23
Detroit River	6	6.77	0.69
Little River	6	6.47	0.55
CONCENTRATED WATER (heated):			
Controls	5	5.72	0.42
Detroit River	6	4.51	0.18
Little River	5	5.19	0.31

Table 10. Effect of several mutagen inhibitors on the SCE levels in C3H mice.

Treatment	Number of Mice	SCE ± SEM
Control (No inhibitor No Cyclosphosphamide)	4	4.36 ± 0.39
Cyclosphosphamide only	4	30.51 ± 0.35
Inhibitor only	4	4.90 ± 0.41
Cyclosphosphamide and Inhibitor	4	25.89 ± 0.10

Table 11. Effects of mutagen promoters on SCE levels induced by CP and MMC.

Promoter	Mutagen	Number of Mice	SCE ± SD
Saline	Saline	6	4.81 ± 0.15
Caffeine	Saline	2*	4.97 ± 0.42
Cyclamic Acid	Saline	3	5.25 ± 0.25
Arsenic	Saline	3	4.88 ± 0.25
Saline	Cyclosphosphamide	3	15.17 ± 0.76
Caffeine	Cyclosphosphamide	3	14.80 ± 0.80
Cyclamic Acid	Cyclosphosphamide	3	12.58 ± 0.76
Arsenic	Cyclophosphamide	3	13.33 ± 0.89
Saline	Mitomycin C	3	17.03 ± 0.43
Caffeine	Mitomycin C	3	21.02 ± 1.60
Cyclamic Acid	Mitomycin C	3	15.20 ± 1.29
Arsenic	Mitomycin C	2	16.70 ± 0.95

* Where less than 3 mice were scored for SCEs deaths had occurred.

TABLE 12. Results of micronucleus analyses in polychromatic and normochromatic erythrocytes of peripheral blood obtained from the suborbital sinus of mice caught in 1986. The last column is a measure of the formation of new erythrocytes.

LOCATION	NO.	DATE OF CAPTURE	MEAN MN-PCE PER 1000PCE	MEAN MN-NCE PER 1000NCE	MEAN PERCENT PCE PER TOTAL
Essex County					
McKim east	18	4/18/86	1.004±1.174*	0.728±0.77	2.714±1.871
McKim west	17	4/25/86	1.685±1.376	0.767±0.553	4.077±2.328
Renaud north	20	5/28/86	0.628±0.784	0.948±0.778	2.708±3.523
Renaud middle	13	5/28/86	2.189±2.404	0.272±0.665	2.142±1.523
Amlin	16	6/6/86	1.894±1.401	0.903±0.766	1.686±1.083
Goolan north	5	6/12/86	0.730±0.732	0.536±0.787	0.536±0.439
Goolan south	7	6/12/86	0.954±1.114	0.933±0.794	1.064±0.637
Holden	8	6/13/86	1.479±1.057	1.090±0.580	1.718±0.795
C. Wilkinson	9	6/26/86	1.378±0.500	1.570±1.153	1.912±1.046
Kent County					
Dilliot	4	5/9/86	0.680±0.844	1.133±1.229	2.168±2.064
Lucio	28	5/23/86	2.720±1.220	0.566±0.814	3.669±2.518
Sheldon	5	5/23/86	1.532±1.494	1.648±2.956	1.504±1.081
Whittington	3	6/9/86	0.903±0.926	0.947±1.125	2.587±1.761
Elgin County					
Oskar	16	6/20/86	0.770±0.758	1.730±1.552	3.629±5.829
Virog	1	6/26/86	3.920	1.450	1.010
Controls					
C3HeB/FeJ	3	5/9/86	2.333±0.586	1.630±0.26	1.593±0.659
	4	5/22/86	1.554±2.055	1.117±0.925	1.830±0.348
	3	5/28/86	2.103±1.489	1.393±1.660	2.683±2.130
	4	6/6/86	2.790±2.500	1.013±0.900	1.513±0.304
	4	6/12/86	2.432±2.094	0.852±0.102	1.215±0.317
	4	6/25/86	1.830±0.794	0.845±0.670	2.385±0.447
	4	6/26/86	0.688±0.863	1.135±0.591	1.795±0.464

* Standard deviation.

TABLE 13: Induction of micronuclei per 1000 cells in peripheral blood of male C3H mice by immersing the mice in a 5% malathion solution or exposing them to benzene vapours.

TREATMENT	NO. OF MICE	MICRONUCLEATED		PERCENT PCEs
		NCEs	PCEs	
Controls	4	0.78 ±1.06*	1.77 ±0.71	1.20 ±0.63
Malathion	4	0.47 ±0.66	1.34 ±1.89	3.50 ±3.40
Benzene	4	1.72 ±1.35	5.79 ±0.64	1.69 ±0.95

* Standard deviation.

TABLE 14: Micronuclei per 1000 cells in peripheral blood of C3H male mice exposed to 15 minutes of shaking per hour for 16 hours, 6 minutes of swimming every two hours for 16 hours or alternating the shaking and swimming hourly. The stress was begun 4 hours after the implanting of the BrdU tablet and continue until the injection of colchine.

TREATMENT	NO. OF MICE	MICRONUCLEATED		PERCENT PCEs
		NCEs	PCEs	
Controls	4	1.22 ±0.52*	2.00 ±0.86	1.61 ±0.33
Shaker only	3	2.18 ±0.69	2.80 ±1.03	1.26 ±0.59
Shaker & Swimming	3	1.15 ±0.57	0.81 ±1.14	2.70 ±2.79
Swimming only	3	1.72 ±1.06	1.11 ±1.34	4.88 ±4.89

* Standard deviation.

TABLE 15: Micronuclei per 1000 cells in peripheral blood of C3H male mice housed in large plastic cages partly filled with corn. Five mice were placed in eachcage. These containers were place in a chrome plating plant within 3 meters of the plating vats. The control mice were housed in a similar container in the animal facility at the University.

TREATMENT	NO. OF MICE	MICRONUCLEATED		PERCENT PCEs
		NCEs	PCEs	
Controls	4	0.23 ±0.45*	2.28** ±2.31	1.44 ±0.34
Chrome plating plant	10	1.69 ±1.16	1.95 ±1.06	2.52 ±0.56

* Standard deviation.

** This high value was due primarily to one mouse which had 5.66 micronucleated PCEs/1000. Without this mouse the count would have been 1.20 ± 0.56.

TABLE 16: Micronuclei per 1000 cells in peripheral blood of C3H male mice receiving 800 mg/kg octachlorostyrene.

TIME AFTER INJECTION	NO. OF MICE	MICRONUCLEATED		PERCENT PCEs
		NCEs	PCEs	
0 hours	4	2.55 ±0.94*	0.98 ±0.77	2.27 ±1.03
48 hours	4	1.86 ±1.04	1.43 ±1.18	3.77 ±3.20
72 hours	4	1.43 ±1.85	1.15 ±0.98	2.50 ±0.94
96 hours	4	2.41 ±1.12	1.93 ±0.99	3.19 ±1.59
120 hours	4	1.12 ±0.50	0.87 ±1.39	3.08 ±1.08
144 hours	4	0.90 ±0.75	0.60 ±0.47	3.45 ±1.23

* Standard deviation.

Field and Laboratory Validation of a HiVol Denuder for Minimizing PAH-Oxidant Reactions During HiVol Sampling

C.S. Davis, R.B. Caton, S.G. Guerin
Concord Scientific Corporation
2 Tippett Road
Downsview, Ontario
M3H 2V2

and

J. Marr, M. Quilliam
Department of Chemistry
McMaster University

INTRODUCTION

Results obtained in a recent study "Evaluation of Alternatives to HiVol Sampling for Polynuclear Aromatic Hydrocarbons", by Concord Scientific Corporation for the Ontario Ministry of the Environment, Air Resources Branch, showed that a denuder efficiently removes ozone from an air stream prior to a HiVol filter (CSC, 1984). In a single experiment, the ozone denuder appeared to reduce on-filter reactions between ozone and captured PAH, as indicated by the significant drop in the number of oxy-PAH species on a protected filter compared to an unprotected filter.

Study Objectives

The objective of this study was to evaluate further the HiVol ozone denuder in terms of mass and the relative attenuation of PAH and PAH derivatives, the effectiveness for removal of NO_2 and HNO_3, and the identification of the oxy- and nitro-PAH contained in the extract of the denuder filter compared to a standard HiVol filter and to determine the lifetime of the denuder bundle. The primary purpose of the program was to identify the chemical species present on the protected versus standard filter and thus determine the effect, if any, of the denuder.

Summary of Experimental Work Program

- The removal efficiencies for NO_2 and HNO_3 by the denuder bundle were determined.
- The lifetime of the denuder bundle, based on the removal efficiency of ozone, was measured during tests of 4 and 6 weeks duration.
- In five warm weather field tests, filters protected by the denuder and unprotected filters, were obtained under selected meteorological conditions that were likely to place the samples downwind of potential PAH sources.
- Dynamic and static laboratory tests in which paired filters (unprotected and denuder-protected) were exposed to known O_3, HNO_3 or NO_2 concentrations were conducted.

MATERIALS AND METHODS

Field Sampling Methods

Four HiVol samplers were used, 2 standard HiVols and 2 denuder-HiVols. All samplers were equipped with electronic flow controllers that maintained a nominal flow of 40 CFM. Flowrates were set initially and checked at the start and end of each field test using a calibrated rotameter. The denuder HiVols were constructed in a fashion similar to that reported in the previous study (CSC, 1984), with minor changes to prevent the bundles from deforming and to allow easier removal of the housing from the HiVol during filter changing. Sampling was performed in Hamilton.

Concurrent ambient levels of particulate nitrate and gaseous nitric acid were measured at the site using parallel 47 mm diameter Teflon filter packs containing a Zefluor 1.0 µm Teflon filter backed up by two Nylasorb filters, at a flow rate of 4.9 L/min. Ambient ozone concentration data during the sampling runs were obtained from the OME station at Barton-Wentworth.

Laboratory Determination of NO_2 and HNO_3 Removal Efficiencies of the Denuder

The effectiveness of the denuder for removing HNO_3 and NO_2 was examined by performing experiments using HNO_3 and NO_2 concentrations as well as relative humidity and temperature levels that were representative of ambient sampling conditions. For the HNO_3 and NO_2 removal experiments, the flow rate through the denuder tube was set as close as possible to the corresponding rate through a single tube (1 Lpm) in the HiVol bundle operating at 40 CFM. The nitric acid removal experiments were conducted at room temperature (~22-24°C) under average (40%) humidity conditions, and at 0°C (100% RH). The apparatus used to perform the experiments (shown in Figure 1) is similar to that used previously (CSC, 1984). Nitric acid concentrations before and after the denuder were measured by ion chromatographic analysis of the extract from nylon fiters placed in the sampling lines.

For the NO_2 removal experiments, a similar apparatus was used.

The NO_2 removal efficiency was determined by difference from measurements of the real-time NO_x levels (Monitor Labs 8840) in the inlet and outlet streams.

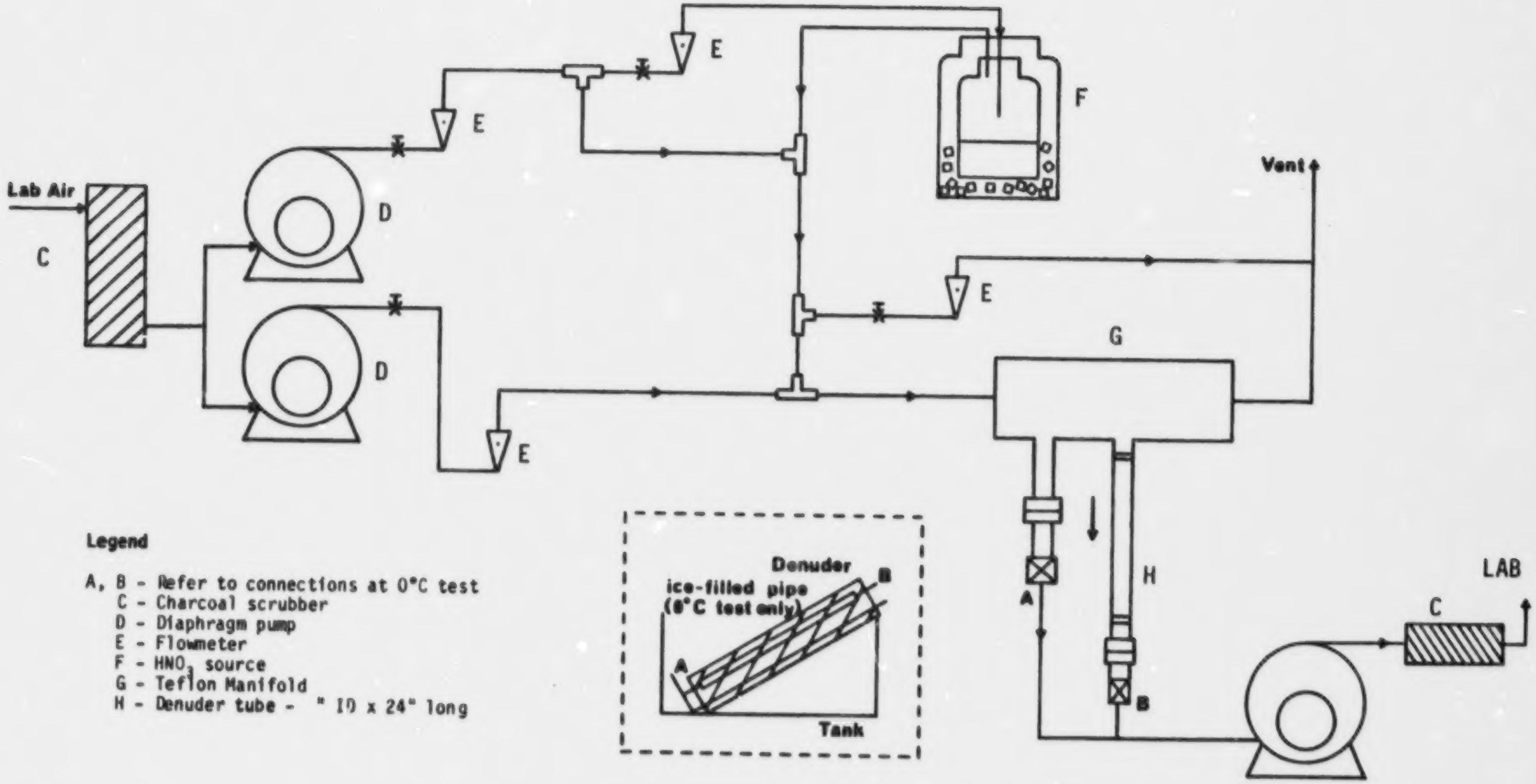
Denuder Tube Lifetime Tests

A denuder HiVol sampler with a fresh denuder bundle was set up on the roof at Concord's head office. After 4 and 6 weeks sampling (not necessarily continuous) at 40 CFM, a different removable tube from the bundle was checked for ozone removal efficiency in the laboratory. A MEC 1000 ozone monitor was used to measure the ozone concentrations entering and leaving the denuder tube.

Ozone and meteorological data (RH, temperature, rainfall only) for the test duration were obtained from OME and the Canadian Climate Centre, for the nearest air quality and meteorological stations. The ozone data allowed calculation of the dose to which then the denuder bundle was exposed.

FIGURE 1

Apparatus for HNO_3 Removal Experiment



Legend

A, B - Refer to connections at 0°C test
C - Charcoal scrubber
D - Diaphragm pump
E - Flowmeter
F - HNO_3 source
G - Teflon Manifold
H - Denuder tube - " ID x 24" long

Laboratory Static and Dynamic Exposure Tests

Sample Collection

HiVol filters were preloaded with particulate matter from ambient sampling. The preloaded filters were exposed to HNO_3, O_3 and NO_2 in a series of laboratory experiments in order to provide exposure conditions that would facilitate identification and analysis of nitro- and/or oxy-PAH products, and also to test the effectiveness of the denuder. The conditions used would therefore of allow extrapolations to indicate what leves of oxy- and nitro-PAH derivatives may be found under ambient conditions.

Static Exposure

Preloaded filters were exposed for 24 hours in a 175 L capacity polyethylene chamber (740 cm x 64 cm x 36 cm) lined with Teflon sheet.

Static Exposures to HNO_3, NO_2 and O_3

A nitric acid vapour concentration (72 ppb) was established in the chamber by allowing a dish (20 cm diameter) containing 25% HNO_3 to equilibrate inside the chamber. NO_2 from a compressed gas cylinder (3.70 ppm NO_2 in air) was passed through the chamber filter. The NO_2 concentration was monitored using a Monitor Labs 8840 NO_x analyser. An ozone generator was used to provide an ozone supply that was diluted with clean air from a compressor. The ozone concentration (250 ppb) was monitored with an MEC1000 ozone monitor.

Dynamic Exposure

Sections of the preloaded filters were exposed to ozone or nitric acid containing air streams. During the exposures, a second section from the same filter was exposed to a reduced concentration by using laboratory scale denuder bundle (CSC, 1984) to remove the challenge gas. Table 1 summarizes the conditions used in dynamic exposure experiments.

TABLE 1

Summary of Conditions Used for the Dynamic Exposure of Preloaded HiVol Filters

Filtered Code	Exposure Conditions	Concentration (ppb)	Time (min)	Flow Rate (lpm)	Volume (m^3)
F9	O_3	200	1440	15	21.6
F10		200	1440	15	21.6
F11		190	1565	15	23.48
F12		200	1440	15	21.6
F13		200	1440	15	21.6
F14		**200→500	1440	15	21.6
F15		200	1650	15	24.75
F16		190	1500	15	22.5
DF9	O_3 Denuder	*30→80	1440	15	21.6
DF10		*15→35	1440	15	21.6
DF11		*25→65	1440	15	21.6
DF12		*35→75	1565	15	23.48
DF13		*20→65	1440	15	21.6
DF14		*10→25	1440	15	21.6
DF15		*10→50	1650	15	24.75
DF16		*25→45	1500	15	22.5
F17	HNO_3	70	1380	15	20.7
F18		60.5	1440	15	21.6
F19		80	1440	15	21.6
F20		43	1800	15	27.0
DF17	HNO_3 Denuder	1.2	1380	15	20.7
DF18		7.5	1440	15	21.6
DF19		1	1440	15	21.6
DF20		1.2	1800	15	27.0
CF21	Control	0	0	0	0

* Concentration at start of run.

** Malfunction caused ozone concentration to rise during run.

Analytical Methodology

Clean-up and Analysis of HiVol Filter Extracts From Field Sampling

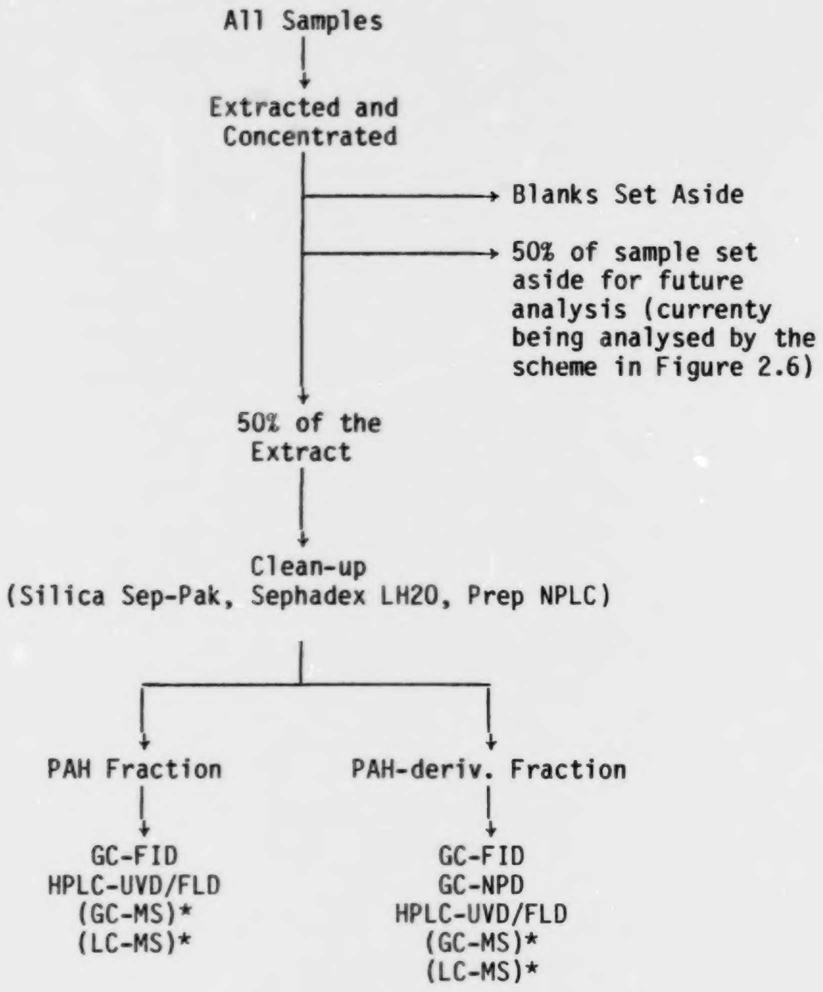
Methylene cloride extracts of the HiVol filters were processed according to a fractionation scheme developed by McMaster University (Quilliam et al., 1984) to give PAH and PAH derivative (e.g., oxy- and nitro-) fractions. GC-FID and/or HPLC analyses were performed on all samples for semi-quantitative analysis and fingerprinting of extracts. GC-MS (or LC-MS) were planned only for those samples representing different samplers, e.g., denuder versus non-denuder, that had significantly differing fingerprints. Pairs of samples were always taken through clean-up and analysis together. Figure 2 depicts the analytical scheme employed. Since there were no apparent differences in the GC and HPLC traces, LC-MS analyses were not done on all samples. One pair of fractions was analysed by LC-MS but no significant differences were observed under the conditions used.

Extraction, Clean-up and Analysis of Static and Dynamic Exposure Experiments

Filters from the static and dynamic experiments were extracted individually (Soxhlet extraction) in a manner similar to that used in the field experiments. The fractionation scheme used for the static and dynamic samples is illustrated in Figure 3. This scheme represents an improvement over the earlier fractionation and analysis scheme in Figure 2 since it provides better precision in the measurement of relative levels of PAH and PAH derivatives. The clean-up scheme was designed to isolate aromatics in the samples from aliphatic and very polar compounds that interfere with the determination. The aromatics from the static experiments samples were analyzed by normal phase liquid chromatography with UV absorption detection (NPLC-UVD) and gas chromatography-mass spectrometry (GC-MS). The aromatics from the dynamic experiment samples were analyzed by NPLC-UVD and normal phase liquid chromatography-mass spectrometry (NPLC-MS). There was not sufficient material in these samples for replicate analyses or for GC-MS analyses.

FIGURE 2

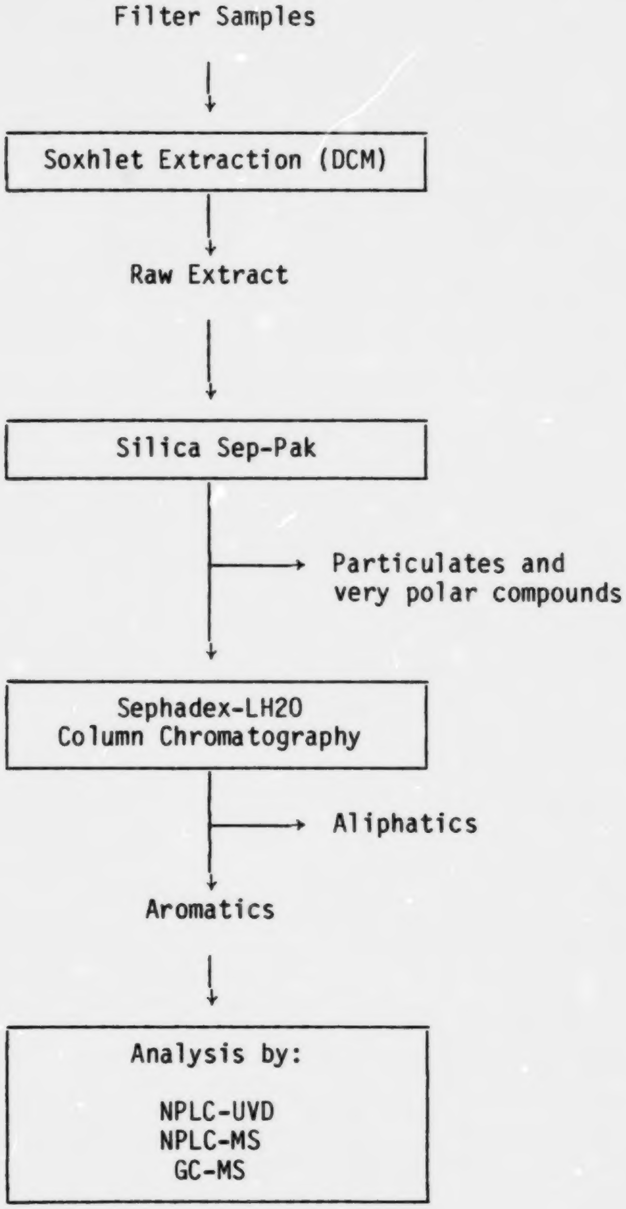
Analytical Scheme for Field Samples


All Samples
Extracted and Concentrated
Blanks Set Aside
50% of sample set aside for future analysis (currenty being analysed by the scheme in Figure 2.6)
50% of the Extract
Clean-up (Silica Sep-Pak, Sephadex LH20, Prep NPLC)
PAH Fraction
PAH-deriv. Fraction
GC-FID
HPLC-UVD/FLD
(GC-MS)*
(LC-MS)*
GC-FID
GC-NPD
HPLC-UVD/FLD
(GC-MS)*
(LC-MS)*

(* Sample set for GC-MS and LC-MS chosen on basis of samples showing greatest differences in GC or HPLC traces)

FIGURE 3

Fractionation and Analysis Scheme for Filters From Static and Dynamic Experiments



RESULTS AND DISCUSSION

Denuder Effectiveness For Removing HNO_3 and NO_2

HNO_3 Removal Experiments

Laboratory tests performed to determine the denuder's effectiveness is removing HNO_3 are summarized in Table 2. Included in Table 2 are the HNO_3 exposure conditions (challenge concentration and duration of exposure) and the nitric and concentration after passage through the denuder (Breakthrough [HNO_3] column in Table 2). The room temperature results showed only marginal breakthrough even though the HNO_3 concentration was 490 $\mu g/m^3$ or ~190 ppb; about one order of magnitude greater than what might be found in polluted atmospheres. Summing the exposures (duration x concentration) in each phase of the test up to breakthrough, indicated a life of 16,500 ppb-hours. This is probably a lower limit since a very elevated concentration was used for the last phase. Assuming 10 ppb ambient HNO_3^- concentration, the denuder would be effective for a time span of 10 weeks.

NO_2 Removal Experiments

Two removal efficiency experiments were conducted, one at ~45% RH and 22°C and the other at ~100% RH and 23°C. Test duration was 24 hours in each case and a fresh denuder tube was used. For the lower humidity test, removal efficiency after 24 hours was only 15% at 72 ppb NO_2, while for the higher humidity test, removal efficiency was 31% at 61 ppb NO_2. Removal efficiency in both cases was only marginally better at the start of the experiment. Since room temperature tests showed that the NO_2 removal efficiencies were poor, it was decided not to pursue tests at 0°C. Any denuder in field use would be required to be effective throughout the entire range of ambient temperatures.

Denuder Lifetime Tests for Ozone Removal Effectiveness

The denuder tube removed after four weeks and six exposure were tested in the laboratory at 23°C and 65% RH for ozone removal efficiency at various challenge ozone concentrations. The test showed removal efficiencies of:

TABLE 2

HNO_3 Removal Experiments

Experiment	Conditions	HNO_3 Exposure	Breakthrough [HNO_3]	Efficiency of Phase
1	23-25°C	Phase 1: after 18.25 hours, 269 $\mu g/m^3$	0	100%
	~40-50% RH	Phase 2: 18 - 42.25 hours, 134 $\mu g/m^3$	<0.7 $\mu g/m^3$	~100%
	0.96 LPM denuder flow	Phase 3: 42.25 - 112.1 hours, 490 $\mu g/m^3$	3.2 $\mu g/m^3$	99.3%
		$\sum$ Phases ≡ 16,500 ppb-hours		
2	~0°C	Phase 1: after 20 hours, 20.0 $\mu g/m^3$	3.1 $\mu g/m^3$*	85%
	~100% RH	Phase 2: after 41 hours, 19.1 $\mu g/m^3$	0	100%
	0.96 LPM	$\sum$ Phases = 310 ppb-hours		

* since Phase 2 showed no breakthrough this result is surprising

25 ppb ≡ 64 $\mu g/m^3$ at 25°C and 101.3 kPa

After 4 weeks

- 100% at 5 ppb ozone
- 80% at 25 ppb
- 65% at 160 ppb
- 60% at 210 ppb

New Tube

- 100% at 155 ppb

After 6 weeks

- 90% at 50 ppb
- 85% at 110 ppb
- 85% at 155 ppb

New Tubes

- 100% at 200 ppb

Estimates of the ozone dose to the denuders (the product of the test duration and the mean ambient ozone concentration) for periods 1 and 2 were respectively 98 and 132 ppb-weeks. On the basis of two data points it is not feasible to establish a correlation between dose and efficiency. However, the data do establish that even after 6 weeks continuous operation, the denuder remained effective (65 to 80% removal efficiency) when challenged with ozone concentrations of ~150 ppb.

Analytical Results - Field Runs

Examination of the chromatograms showed that only one field run S3 showed minor differences between the standard and denuder sampler systems. Several PAH compounds were identified in the PAH fraction from the standard HiVol and the denuder HiVol filter extracts in run S2. Identification was by comparison of UV-visible spectra of the HPLC fractions with that of standards. The reproducibility of most analyses between duplicate samples was sufficiently good to suggest that any significant difference would have been observed readily.

The data were somewhat surprising, i.e., there appeared to be little impact of the denuder. There are three possible explanations for the lack of difference:

- the denuder was not effective,
- there was little artifact formation occurring in the particulates during sampling,
- any artifact formation had already occurred in the atmosphere.

In view of this the static and dynamic laboratory exposures of precollected samples were conducted.

Static and Dynamic Laboratory Exposure Tests

All extracts from similarly treated filters were pooled, eight samples were generated, namely, 4 from the static experiments (from control, ozone nitric acid and nitrogen dioxide exposed filters) and 4 from the dynamic experiments (standard and denuder protected from nitric acid and ozone exposure).

The aromatics from the static experiment samples were analyzed by normal phase liquid chromatography with a UV absorption detector (NPLC-UVD) and gas chromatography-mass spectrometry (GC-MS) using the cleanup scheme shown in Figure 3. The aromatics from the dynamic experiment samples were analyzed by NPLC-UVD and normal phase liquid chromatography-mass spectrometry (NPLC-MS). There was not sufficient material in these samples for replicate analyses or for GC-MS analyses.
The data from the NPLC-MS analyses were examined by plotting the mass chromatograms of various PAH and PAH derivatives, normalized with respect to that of 276-PAH which acted as an internal standard to correct for volumetric errors and which was assumed not to undergo transformation (or transformation to similar extents) when unprotected by the denuder. Peak areas from the mass chromatograms of the standard and denuder samples were incorporated in the following equation for a "noramlized ratio".

Normalized Ratio =

$$\left(\frac{\text{Area of M of standard HiVol}}{\text{Area of M of denuder HiVol}}\right) \times \left(\frac{\text{Area of M 276 peak from denuder HiVol}}{\text{Area of M 276 peak from standard HiVol}}\right)$$

If there were no differences between the standard and denuder samples, this ratio should be 1.00. However, if there were certain PAH converted to PAH derivatives, the ratio for the PAH would be less than 1.00, while that of the derivatives would be greater than 1.00.

Static Experiments

There were no apparent differences in the NPLC-UVD or GC-MS traces between the control sample extract and the extracts from the filters exposed to ozone, nitric acid or NO_2. It is likely that the dose (concentration x exposure duration) was insufficient to cause discernable reactions of the filters.

Dynamic Experiments

Analytical data for the four pooled samples are given in Table 4. Peak areas for identified PAH and ketone as well as quionone PAH derivatives in the standard (STD) and denuder protected (DENUD) filter extracts are listed for the ozone and nitric acid experiments. The normalized ratios for the standard to the denuder-protected peak areas for each compound are also indicated.

The effectiveness of the denuder will be indicated by
a) the appearance of different species in the standard versus the denuder protected samples, and/or
b) differences in the amounts of PAH derivatives and/or PAH compounds.

Ozone Exposure

The NPLC-UVD analyses showed that there were no major differences in the standard and denuder-protected samples, i.e., no new compounds (extra peaks) appeared in the standard versus the denuder-protected chromatograms. Dramatic differences were observed in the NPLC-MS data of the ozone samples. Compounds in the PAH derivative region showed normalized ratio values significantly greater than 1.00 (2 to 10), which means they were at a higher concentration in the standard sample versus the denuder sample. The mass spectra of these PAH derivaties show losses of 28 mass units from the molecular ion, which indicated that they are ketone and quinone derivatives of PAH. Positive identification of these compounds was not possible.

The data in Table 4 also show that the concentrations of some PAH are significantly lower in the ozone standard sample, which could be the result of reaction of these PAH with ozone to give the observed PAH-derivatives and other undetected products. It is useful to note that

TABLE 4

Analytical Results From LC/MS Analyses of Pooled Dynamic Samples

			Ozone Dynamic Peak Area			Nitric Acid Dynamic Peak Area		
Compound Identity	M/Z	Scan #	STD	DENUD	Norm.* Ratio	STD	DENUD	Norm. Ratio
Phenanthrene	178	354	3859	20898	.4	25094	30590	.7
Fluoranthene	202	371	3846	15341	.5	28140	25788	.9
Pyrene	202	378	5911	23824	.5	37301	?	
Benzofluorenes	216	378	706	4340	.4	?	?	
264-PAH	264	379	194	786	.6	?	?	
266-PAH	226	389	1773	6475	.6	24101	?	
240-PAH	240	397	796	2135	.8	?	?	
265-PAH	264	397	542	1052	1.2	?	?	
Benz(a)anthracene	228	398	7864	25639	.6	66726	62832	.9
Chrysene	228	402	1987	5605	.7	17850	18226	.8
240-PAH	240	402	683	1980	.8	?	?	
252-PAH	252	413	35443	77576	1.0	140710	153793	.7
264-PAH	264	415	1480	3068	1.1	?	?	
276-PAH	276	427	3342	75267	1.0*	176837	163050	1.0*
278-PAH	278	429	7464	14301	1.1	27965	31214	.7
Anthraquinone	208	577	1929	?		14339	14374	.8
?	226	677	4438	2229	4.4	9571	7221	1.1
230-PAK	230	500	4055	5364	1.7	33364	39760	.7
230-PAK	230	534	1080	1260	1.9	3952	4343	.7
230-PAK	230	618	7628	5862	2.9	41641	48755	.7
230-PAK	230	648	7531	5649	3.0	33061	30413	.9
254-PAK	254	508	746	1323	1.2	45504	4077	.9
254-PAK	254	586	2862	?		7534	6862	.9
254-PAk	254	608	3365	2824	2.6	8396	8952	.8
254-PAK	254	638	1433	644	5.0	?	?	
254-PAK	254	677	14787	9821	3.3	37052	29983	1.0
258-PAQ	258	536	3556	3394	2.3	12671	13664	.8
258-PAQ	258	600	2357	546	9.7	6924	7584	.7
278-PAK	278	606	5458	4398	2.7	13130	13128	.8
278-PAK	278	628	1197	412	6.5	2686	2558	.9
282-PAQ	282	639	3333	1381	5.4	9420	9280	.8
1-Nitropyrene	247	465	2234	3189	1.5	3288	3505	.8
Nitrofluoranthene	247	476	499	1064	1.0	2623	3726	.6

* The 276-PAH peak was used as an internal standard to derive the normalized ratio $(Asj/Adj)x(Ad_{276}/As_{276})$, where A = area, s = standard hivol, d = denuder hivol, j = peak of interest, and 276 = 276 PAH.

the compounds with saturated carbons, such as the benzofluorenes (MW 216), are most susceptible to oxidation, and have low ratios though not exclusively so. The low normalized ratio for the PAH compounds could be due to evaporative losses, but this can be ruled out since both samples were subjected to similar airflows, both during initial sample collection and during the dynamic exposure tests. In addition, care was taken to ensure that sample pairs were treated similarly during the cleanup procedures so that evaporative losses were minimised.

Nitric Acid Exposure

NPLC-UVD and NPLC-MS data did not indicate differences between the standard and the denuder-protected samples in the dynamic nitric acid exposure experiments. The levels of the oxy-and nitro-PAH were similar in both types of samples.

These results point to one or more of the following possibilities

a) the dynamic exposure conditions were inappropriate to effect nitration reactions

b) the reactions did occur, but the denuder afforded no additional protection

c) nitration reactions occurred prior to the dynamic exposure i.e., during sample collection

Examination of Table 4 shows that while the levels of the 1-nitropyrene were similar in the nitric acid exposure runs, the 1-nitropyrene level in denuder-protected sample of the ozone run was surprisingly higher than that for the standard HiVol. The converse was true for nitrofluoranthene i.e., similar levels for standard and denuder protected samples in the ozone experiments but higher levels for the denuder protected samples in the nitric acid experiments. The explanations for these results are not clear and on the basis of two pairs of samples, speculation about likely explanations are inappropriate.

SUMMARY AND CONCLUSIONS

The experimental data from this study have shown the following:

1. The denuder is effective not only for ozone, but also for nitric acid. Breakthrough of HNO_3 was found to occur only after 16,500 ppb-h exposure. Assuming ambient nitric acid concentrations of 10 ppb, the estimated lifetime for nitric acid would be 1650 h or ~70 d continuous operation. Within these limits, the removal efficiency for HNO_3 was >99% at room temperature and >85% at 0°C.

2. After 42 days continuous field operation with a mean ozone concentration of 22 ppb, equivalent to an ozone dose of 23760 ppb-h, the denuder's efficiency for removing ozone was 85% for a laboratory ozone challenge concentration of 155 ppb and 90% removal efficiency for 50 ppb.

3. Analysis of extracts from standard and denuder HiVol field samples showed insignificant differences in the PAH derivative composition. The concurrent ozone and nitric acid concentrations during the field runs were not exceptionally high (O_3 daily maximum in the range of 40-66 ppb and 24h average HNO_3 2-5 ppb). The O_3 and HNO_3 levels however are typical of the majority of non-episodic days.

4. Laboratory tests showed that the denuder reduced the formation of oxygenated PAH derivatives within fairly broad analytical uncertainty. Ozone concentrations to which standard, i.e., unprotected, filters were exposed were ~200 ppb.

5. Dynamic laboratory tests in which preloaded filters were challenged with nitric acid - in one case directly and in the other case protected by the denuder, showed no differences in the PAH derivative fractions between samples.

6. Analogous tests on filters using static exposure conditions for O_3, HNO_3 and NO_2 separately showed no differences in the PAH derivative fraction compared to control filters.

The apparent lack of reaction with nitric acid is surprising but conflicting results regarding the nitration of PAH are found in the literature.

Although several investigators have studied the reactions of PAH with potential nitrating agents such as NO (Hughes et al., 1979), HNO_2 (Lindskog, 1983), NO_2 (Grosjean et al., 1983; Pitts et al., 1978) and N_2O_5 (Pitts et al., 1985), the most likely nitrating agents appear to be N_2O_5 (Pitts et al., 185) or HNO_3 (Grosjean et al., 1983). Conclusive evidence regarding the extent to which nitration of PAH in ambient sampling remains to be demonstrated.

REFERENCES

Anlauf, K.G., Fellin, P. and Wiebe, H.A. 1984. Characterization of several integrative sampling methods for atmospheric particles, nitric acid and sulphur dioxide. Report ARQA 117-84, Atmospheric Environment Service, Downsview, Ontario.

CSC, 1984. Concord Scientific Corporation report 110.J212 "An Evaluation of Alternatives to HiVol Sampling for Polynuclear Aromatic Hydrocarbons" for Ontario Ministry of the Environment, Air Resources Branch, March 1984.

Grosjean, D., Fung, K. and Harrison, J. 1983. "Interactions of Polycyclic Aromatic Hydrocarbons with Atmospheric Pollutants", Environmental Science and Technology, Vol. 17, No. 11, 673-679, 1983.

Grosjean, D. 1983. "The effects of nitrogen dioxide and ozone on the decomposition of particle associated polycyclic aromatic hydrocabons during sampling from the atmosphere. Author's reply," Atmos. Environ. 17:2112.

Hughes, M.M., Natusch, D.F.S., Taylor, D.R., Zeller, M.V. 1979. "Chemical transformations of particulate polycyclic organic matter," in Polynuclear Aromatic Hydrocarbons: Chemistry and Biologicl Effects, Fourth International Symposium, A. Bjørseth and A.J. Dennis, eds., Battelle Press, pp. 1-8.

Mukammal, E. 1984. Report on oxidant climatology of Ontario. Canadian Climate Centre, Application and Impact Division, Atmospheric Environment Service, Environment Canada.

OME, 1984. Acid Precipitation in Ontario Study. Cumulative Ambient Air Concentrations Listings August 31, 1981 - January 4, 1983. Ontario Ministry of the Environment Report, ARB-145-84-ARSP API 013/84.

OME, 1985. Air Quality Monitoring Report, Ontario, 1983. Ministry of the Environment Report ARB-104-85-AQM.

Pitts, J.N., Jr., Van Cauwenberghe, K.A., Grosjean, D., Schmid, J.P., Fritz, D.R., Belser, W.L. Jr., Knudson, G.B., and Hynds, P.M. 1978. "Atmospheric reactions of polycyclic aromatic hydrocarbons: facile formation of mutagenic nitro derivatives," Science 202:515.

Pitts, J.N., Jr., Likensgard, D.M., Ripley, P.S., Van Causwnberghe, K.A., Van Vaeck, L., Shaffer, S.D., Thill, A.J., and Belser, W.L., Jr. 1980. "Atmospheric epoxidation of benzo[a]pyrene by ozone: formation of the metabolite benzo[a]pyrene-4,5-oxide," Science 210:1347.

Pitts, J.N., Jr., Zielinska, B., Sweetman, J.A., Atkinson, R. and Winer, A.M. 1985. "Reactions of adsorbed pyrene and perylene with gaseous N_2O_5 under simulated atmospheric conditions," Atmospheric Environment 19(6):911-915.

Quilliam, M.A., Marr, J., and Gergely, R.J. "Analysis of Polycyclic Aromatic Hydrocarbons and Their Derivatives in Environmental Samples," in Proceedings of the Technology Transfer Conference No. 5, Nov. 22, 28, 1984, Toronto, Ontario, Part 2: Air Pollution Research, pp.903-924. Research Advisory Committee, Policy and Planning Branch, Ontario Ministry of the Environment.

A PARTICLE-SIZE SPECIFIC ELEMENTAL MASS BALANCE FOR APPORTIONMENT OF AMBIENT AEROSOL SAMPLED WITH MULTISTAGE FRACTIONATORS

T.G. Pringle and R.E. Jervis
Department of Chemical Engineering and Applied Chemistry,
University of Toronto, Toronto, Canada M5S 1A4

ABSTRACT

Photon and thermal neutron activation analysis were used to determine the concentrations of up to thirty elements in aerosol samples collected by cascade impactor in Toronto, Canada during the period July to December of 1985. Examination of the particle-size distributions thus obtained led to the development of a new receptor model. A size-specific elemental mass balance was used to apportion the mean ambient Pb aerosol concentration amongst four contributing sources as follows: secondary lead refinery emissions (46%), refuse incineration (28%), automotive exhaust (25%) and re-entrained soil and dust (<1%). The predicted concentrations of Al, As, Br, Na, Pb, Sb, and Zn agreed with observed concentrations to within a factor of two for most elements in most particle size fractions.

INTRODUCTION

Increased use has been made during the last decade of receptor models to identify aerosol sources and to apportion ambient particulate matter among a set of contributing sources. /1,2/ Such models utilize as input data a set of aerosol measurements made at a particular sampling location (receptor site) and include as parameters, some or all of: chemical composition, particle-size distribution, site location and meterological data, in attempts to resolve statistically the major emission sources contributing to ambient particulate matter at that site. This method is considered less capital-, manpower- and time-intensive than alternative, much-used approaches of coupling aerosol emission inventories with dispersion models to achieve similar results.

In a previous study, Pringle and Jervis /3/ performed factor analysis upon a data set containing the concentrations of 15 chemical elements in 18 airborne particulate matter samples and were able to identify the primary aerosol sources at a site in Port Credit, a relatively non-industrial satellite town of Toronto, Canada. Five emission sources contributing at that location were labelled as: soil, transportation vehicles, refuse and oil combustion, winter road salt and, one unidentified arsenic source, and these sources had been resolved through factor analysis and their relative contributions to the ambient aerosol determined through the use of a chemical mass balance (CMB) receptor model.

A major limitation of this method of source apportionment in highly industrialized areas is the inability of the CMB model to differentiate between aerosol sources which have similar chemical compositions (in terms of interelemental concentration 'profiles'), viz.refuse incinerators, automobile emissions and non-ferrous industries such as zinc and lead processors. To overcome some of these limitations in the methods, a modified approach has been used in the research presented here: the particle-size distributions of ambient particulate matter are measured and differences in size distribution, for certain elements among emission sources, are utilized to separate 'elementally-collinear' sources.

Whereas several (other) published studies /4,5,6/ have indirectly made use of particle-size data by separating the aerosol into coarse and fine fractions (<2.5 µm, 2.5-10 µm), which data is then used separately in receptor modelling, the objective of the present study was to divide the aerosol into multiple size fractions so that unique aerosol size-distributions were not lost by separation, during sampling, only into two fractions.

There are several requirements of the analytical procedures that are chosen for use in receptor studies: the technique chosen must be able both to to determine as many of the chemical elements as possible in particulate samples small in mass and also be capable of determining many of the 'key ' marker' elements which help distinguish different sources contributing to the aerosol collected at the receptor site. Furthermore, because of the statistical nature of the modelling procedures, variance in the experimental results due to the analytical techniques themselves, must be minimized. A sensitive multielemental instrumental method such as activation analysis is ideally suited to meet these requirements; in this work, a complementary coupling of thermal neutron and photonuclear activation techniques allowed determination of most elements of interest as well as permitting two independent determinations for a subset of elements as a means of data quality control./5/ Further, in this study, when individual aerosol size fractions contained as little as one tenth of the total mass of particulates collected, the use of the activation technique was even more essential as a means to obtain the necessary analytical results for practical modelling.

MATERIALS and METHODS

A series of samples of airborne particulate matter was collected at regular intervals during the period July-December, 1985 using Anderson and Sierra high-volume cascade impactors deployed in central Toronto, Canada. The samplers were operated for 12 hour periods at a regulated flow-rate of 0.019 m^3s^{-1} (or, 40 scfm) and filtered a total air volume of approximately 820 m^3. By means of the Sierra 235 and Anderson Hi-vol impactor heads, the airborne particulate was separated during collection into 5 or 6 size fractions according to their aerodynamic diameters. Scanning electron microscopy (SEM) and elemental analyses performed on typical aerosol specimens indicated that large particle 'bounce-off' from upper stages - a phenomenon at question with some cascade impactors - was less pronounced for the Sierra 235 impactor than for the Anderson instrument. A prior soaking of the collection substrates in a Vaseline/hexane (1:10) solution, repeated several times, further improved particle retention on the impactor upper stages so that the particle-size distribution determined by direct examination with SEM was found to be quite close to the manufacturer's specified stage particle-size cutoffs, viz. 7.2, 3, 1.5,0.95 and 0.49 µm at 50% collection efficency, with a 'backup' filter used to collect all remaining particles of lower diameter in the incident airstream. Whatman # 41 cellulose filter material was chosen as the collection medium both for the substrates in the several impactor stages and for the 'backup' filters because of its low trace element content and its structural integrity when moist. Glass fibre material, the standard aerosol filter medium, was considered particularly unsuitable as a substrate for activation analysis because of high Na and ash content.

After particulate sample collection, each substrate was halved and the edges trimmed to remove any contamination from handling or contact with the sampler. A half section of each was analyzed by photonuclear activation analysis(IPAA) at the National Research Council (Canada) electron linear accelerator facility (LINAC) in Ottawa. The remaining half section was subjected to neutron activation analysis (INAA) at the University of Toronto SLOWPOKE-2 nuclear reactor facility. Backup filters were divided into four sections, trim-

---

[1] Sierra 235 and Anderson Hi-vol impactor heads are products of Anderson Samplers Inc.

Table 1

MEAN ELEMENTAL CONCENTRATIONS OF AIRBORNE PARTICULATE MATTER (ng.m^{-3})

Element	Toronto (this study)	Toronto Suburb (1985)/3/	Washington (Kowalczyk et al,1982)/8/	Chicago (Scheff et al,1984)/4/
Al	1100 ± 420	600	1350 ± 110	1630 ± 900
As	4.6 ± 6.7	5.3	3.25 ± 0.2	4.3 ± 4.7
Br	61 ± 28	70	136 ± 9	-
Ca	4150 ± 1780	2150	860 ± 40	3420 ± 3290
Fe	1150 ± 670	640	1000 ± 60	2310 ± 1530
Mn	49 ± 28	34	17 ± 2	89 ± 71
Na	850 ± 540	1520	300 ± 20	2540 ± 2480
Pb	1100 ± 1510	300	440 ± 20	490 ± 230
Sb	11.3 ± 17	-	2.1 ± 0.2	-
Sc	0.2 ± 0.08	0.13	0.33 ± 0.03	-
Ti	100 ± 60	64	110 ± 10	-
V	3.8 ± 2.9	5.9	25 ± 2	8.74 ± 6.39
Zn	640 ± 1040	108	85 ± 6	304 ± 288
n(no.of samples)	8	18	130	35

med and two sections each were subjected separately to (duplicate) IPAA and INAA. Complete details on the experimental procedures, irradiation parameters, accuracy and interferences relevant to the analysis of particulate matter and similar materials by IPAA and INAA have been reported previously. /3,7/ By use of a 35 MeV electron energy and typical range of beam currents of 30-60 µA, Pb,Zr,Ca,Ti,Sb and As could be determined, of which Pb, Zr and Ti were not measured with acceptible precision by INAA; other elements among these were used for accuracy checks between the two techniques.

The other sections of each particulate sample were then subjected to sequential thermal neutron irradiations for periods ranging from 2 min. to 16 h, for determination using short-lived nuclides of: Al,Ca,Cl,Cu,I,In,Mn,Ti,V; and using longer-lived nuclides: Ag,As,Br,Ce,Co,Cr,Cs,Eu,Fe,Hf,K,La,Sb,Sc,Sm,Th,W and Zn. Irradiations were at neutron fluxes from 2.5-10 x 10^{15} $m^{-2}s^{-1}$ and Ge-gamma-spectrometry performed at periods from 1 min. to 60 d.

A U.S. Nat. Bureau of Standards reference material coal, 1632a bituminous coal, was used as a multielemental standard both for IPAA and INAA. Since the samples and standards were quite different in volume and shape, care was taken to spread the standard to extend over a volume equal to that of the folded filter samples and this was accomplished by placing a known small quantity of the standard in each of several polyethylene capsules. Other standards: NBS air particulate reference material, SRM 1648 and flyash, SRM 1633a, were used also to verify analytical accuracy which was found to be, typically ±10% between reference materials.

RESULTS and DISCUSSION

The mean concentrations of a selection of sixteen of the chemical elements measured in airborne particulate matter from Toronto, Canada during a mid-1985 sampling period are presented in Table 1. Although the concentrations of 30 elements were determined, those listed and included in the calculations presented here were considered to be the most useful for the purpose. A complete tabulation of results will be given in a forthcoming report. /8/ Presented also in the table for comparison are aerosol concentrations from recent studies

FIGURE 1

TYPICAL PARTICLE-SIZE DISTRIBUTIONS IN THE TORONTO AEROSOL

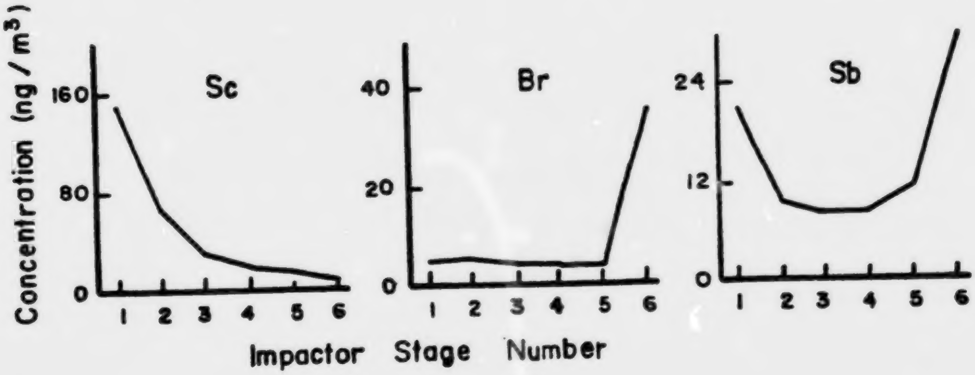
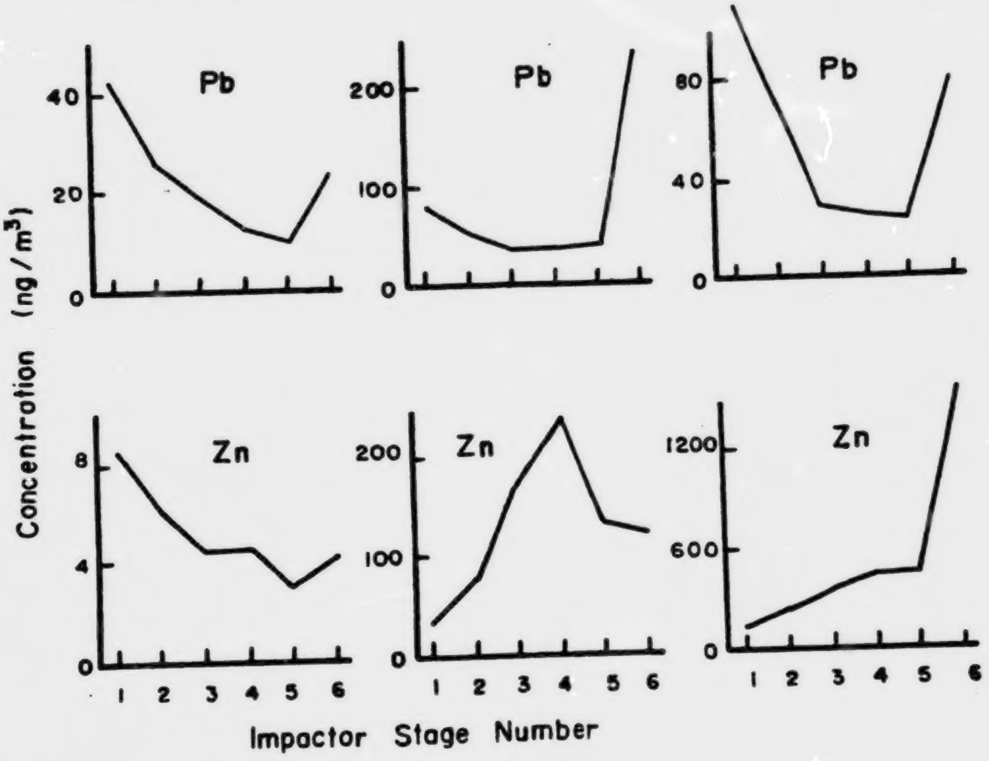


FIGURE 2

LEAD AND ZINC PARTICLE-SIZE DISTRIBUTIONS: INDIVIDUAL SAMPLES



in a Toronto suburb by Pringle and Jervis /3/, Washington /9/ and Chicago /4/.

Compared to the relatively-low concentrations found in the previous Toronto study /3/, the present results indicate levels of most elements which are similar to those reported for the two U.S. cities. However, the present measurements were made in a more industrialized area than the 1985 study and there was no snow cover to reduce soil entrainment, as there was in the earlier study. By way of comparison with relatively non-industrial Washington, most elemental concentrations are higher in this study although still less, in most cases, than those from Chicago, a much more heavily industrialized city.

It is assumed that the higher Ca values for Toronto were a result of a strong limestone component in local soils and rocks and that lower amounts of Br indicated a higher ratio of unleaded to leaded gas. The significantly higher concentrations of Pb, Sb and Zn were assumed to arise from local industry and the relatively large standard deviations for those elements to be caused by the coincidence of daily wind changes with a 12 hour sampling period which tended to reduce time-averaging of emissions from local point sources of aerosol.

Size Distributions

As was the case for the previous Toronto study, all of the elemental size distributions were classified by their shape as belonging to one of three groups. Figure 1 illustrates this classification with elemental concentration plotted against impactor stage number; stages 1 to 6 represent effective particle cutoff diameters of 7.2, 3, 1.5, 0.95, 0.49 and <0.49 µm, respectively.

The elements K, Al, Ca, Fe, Sc, Ti and Th all had a particle-size distribution profile which consisted primarily of large particles, similar to the profile for scandium in Figure 1. This group of elements is commonly associated with soil particles /4,9,10/ and their relatively large particle size indicates a physical entrainment process. This size profile was therefore considered to be that of re-entrained soil and dust. In contrast, the elements Br and I, as well as Pb, Sb, Zn and Cl in a few samples, possess particle-size profiles which show a predominantly fine-particle bias. These elements are associated with combustion processes such as automotive exhaust (Br), refuse incineration (Zn, Pb, Sb) or coal combustion (I) and their profiles are indicative of combustion vapour phase emissions which have condensed on fine particles. /11/

Most of the remaining elements (As, Mn, V, Se, Na as well as Pb, Sb, Zn in some samples) have size distributions which resemble the Pb profile in figure 1 in that they show pronounced elevations in concentration for both small and large particles, indicating some combination of both soil entrainment and combustion as the aerosol source. The profiles for Zn, shown in Figure 2 are unusual since they indicate that there might be three different source mechanisms for the emission of zinc-bearing particles with a predominance of either of large, medium or small particles. It was felt that this type of difference could be exploited to separate the emissions from several sources of aerosol which have similar elemental compositions.

Receptor Model Application

In the 1985 study of a Toronto suburb, two receptor models were used, factor analysis and a chemical mass balance (CMB). Both are based on equation (1) where the observed concentration of element i (a_i) is assumed to be the

$$a_i = \sum_j b_{ij}c_{ij} \tag{1}$$

linear sum of the contributions from j sources. In factor analysis, a matrix (A, n x i) of i elemental concentrations in n samples (a_{in}) is reduced to a matrix of j hypothetical vectors (B, i x j) such that a maximum of the variance in A is reproduced by the new matrix. The elements which are most strongly associated with each new vector (b_j) served to identify that vector, or "source", by their common associations. Thus the number and type of major aerosol sources contributing to the ambient aerosol can be determined with no a priori assumptions. With this information, the elemental composition of emissions from each source can be approximated (c_j) and, using least squares regression to solve equation 1 for i elements in each sample, the contribution of each

TABLE 2

ELEMENTAL SOURCE PROFILES (μg/g)

Element	Soil	Automotive Sources	Refuse	Refinery Emissions	Z1	Z2	Road Salt
Al	50000	700	14000	3000	3600	36000	0
As	10	0	200	2600	120	120	0
Br	31	45500	1000	54	44	44	750
Ca	76000	1700	17000	4700	700	700	6000
Fe	30000	2000	6500	11000	4000	4000	0
Mn	650	1500	730	540	300	300	0
Na	26500	0	82000	10000	2200	2200	350000
Pb	200	130000	75000	160000	3400	3400	0
Sb	9	0	1500	7600	15	15	0
V	60	0	100	25	30	30	0
Zn	200	1000	120000	2400	150000	150000	0

source to the ambient airborne particulate matter (c_j) can be calculated.

It has been noted /4,12/ that receptor models are unable to reliably separate sources of similar elemental composition (collinear sources). In factor analysis a knowledge of possible contributing sources is necessary to realize that a pair of collinear sources exist since only one eigenvector will exist for that pair. In the CMB, either one elemental profile is used for both sources or the least-squares regression will cause one source to have a large positive contribution to the aerosol and the other to have a large negative contribution and so provide the best possible fit.

This is not a serious problem in a lightly industrialized city; the only pair of elementally collinear sources modelled by Kowalczyk et al /13/, in their study of aerosol in Washington, D.C., was coal flyash and soil and they were able to use Mn and As to help differentiate between the two sources. However, in the industrialized area where the present study was conducted there are many local industrial sources. For example, a secondary lead refinery, two municipal incinerators and two high traffic-volume roads all contribute to the Pb concentration in the ambient aerosol. Here, instead of the traditional approach mentioned above, the CMB was altered so that each elemental concentration (ai) in equation (1) was replaced by the six concentrations of that element in the six separate particle-size fractions (a_i1, a_i2,.... a_i6) collected by cascade impactor. In effect, the several sources which rely on a particular marker element, Pb in this case, can be separated by their respective particle-size profiles. In order to test this new model concept, an attempt was made to calculate the contributions of various sources to the ambient Pb aerosol. To reduce the number of assumptions required in the model, a subset of elemental and particlesize data was composed such that only marker elements and particle-size profiles for major sources of Pb were considered along with markers which strongly affect calculations for these sources.

Although factor analysis was employed to identify the major contributing sources of aerosol in the previous Toronto study, this was not overly useful in the present research since, where several sources have collinear composition profiles only the sources with with the largest concentration variations, would be identified. Variations in the lead refinery emissions were much greater in all size fractions than those for the other sources of Pb. Furthermore, only eight samples were analyzed for this study, too small a number for all but the grossly varying sources to be identified.

The composition of the data subset was determined by examination of the particle size profiles and a review of the literature to examine likely elemental profiles /2/. For example, from Figure 2 the lead aerosol size distribution

TABLE 3

PARTICLE-SIZE PROFILES FOR VARIOUS SOURCES (% OF TOTAL CONCENTRATION)

Impactor Stage No.	ECD (μm)	Soil, Salt	Auto	Refuse, Z1	Refinery Emissions	Z2
1	7.2	51	9	13	28	4
2	3	25	12	14	14	10
3	1.5	11	10	8	10	21
4	0.95	7	9	12	9	31
5	0.49	4.5	7	11	9.6	17
Backup Filter	<0.49	2	54	42	30	16

TABLE 4

PREDICTION AND APPORTIONMENT OF LEAD AEROSOL

	Mean Source Contributions (ng m^{-3})				Total Concentration (ng m^{-3})	
Element	Soil	Automotive Emissions	Refuse	Refinery Emissions	Predicted	Observed
Al	1060	0.9	27	5	1090	1100 ± 420
As	0.2	0	0.4	4.3	5.8	4.6 ± 6.7
Br	0.7	57	1.9	0.1	60	61 ± 28
Na	550	0	157	17	780	850 ± 540
Pb	4.2	163	144	264	575	1100 ± 1510
Sb	0.2	0	2.9	8.3	11.3	11.3 ± 17
Zn	4.2	1.3	230	4	240	638 ± 1040

appears to be the result of a combination of two sources, one composed of predominantly large particles and one of predominantly small particles. However, consideration of the possible sources of lead and of ratios between lead and other common marker elements in these sources, such as Al (soil), Br (automotive emissions) and As and Sb (lead alloying operations) /10/ indicates that four sources of airborne lead exist : large particle lead from soil, small particle lead from automobiles and refuse incineration and a combination large-and-small profile from the secondary lead refinery which was indicated by high correlation coefficients between Pb, As and Sb.

The chemical composition profiles for the sources considered are listed in Table 2 and the particle-size profiles are listed in Table 3. The actual model profiles were calculated by the combination of these two matrices. The soil size profile was obtained from the particle-size distribution of Sc since there are no major anthropogenic sources of this element. Aluminum size distributions were very similar indicating agreement and, by their lack of a large fine particle component, also indicating little evidence of coal combustion products. The elemental profile was obtained from analysis for 32 elements in over 50 soil and dust samples from throughout Metropolitan Toronto. /13/ The automotive elemental profile was derived from the literature /2/ and Pb/Br ratios from aerosol samples with little evidence of industrial contribution. The size profile for automotive emissions was determined from Pb and Br measurements on Toronto Island, aerosol samples from which show a strong Pb/Br correlation. It was assumed that, due to wind direction and sheer mass of the auto emission component, any confounding sources of Pb or Br were negligible.

TABLE 5

MASS BALANCE L/S RATIOS

Element	4 Sources Separate Sizes	4 Sources Total Aerosol	7 Sources Total Aerosol
Al	1.8	1.01	1.33
As	1.9	1.26	1.19
Br	1.2	1.02	1.04
Na	1.4	1.09	1.02
Pb	1.7	1.9	2.0
Sb	1.6	1.0	1.02
Zn	2.2	2.7	1.2
Average	1.7	1.4	1.26

Pb/Al and Br/Al ratios for island soil /10/ were used to remove that component before profile calculation. The zinc in the automobile componemt, assumed to be from tire wear, was given a size profile similar to the soil profile, indicating erosion followed by dust entrainment rather than combustion. With this one exception, it was necessary to make the simplifying assumption that elemental ratios remained constant for all aerosol sizes from a given source; this was the result of a lack of available literature information.

The chemical profiles for refuse incineration and lead refining were obtained from a compilation of source profiles. /2/ The size profiles for lead refinery emissions were obtained from those of As since Pb, As and Sb were strongly correlated at the refinery site and because there were no other major sources of As indicated.

Source Contributions

Table 4 lists the mean contributions of the four major sources of Pb aerosol to the ambient airborne particulate matter. These were obtained by least squares regression of the measured concentrations with the combination particle size and composition profile. Following a suggestion by Kowalczyk et al /12/,each elemental size fraction was weighted by $1/s^2$ where s is the analytical error in each concentration determination. This permits the CMB to weight all elements according to their analytical precision rather than according to the magnitude of their absolute concentrations.

The secondary lead refinery contributes the largest amount of airborne Pb, with a mean contribution of 46%. Airborne soil and dust particles contribute the least (<1%) with automotive emission and refuse incineration contributing approximately 25% and 28% respectively. The larger/smaller ratio in Table 4 is the larger of either the predicted-to-observed or observed-to-predicted ratio. The use of L/S ratios avoids the balancing of gross overpredictions and underpredictions and is thus a better measure of the balance fit. /6 The L/S of 1.9 for lead is an indication either that the profiles for lead are slightly inaccurate or that other sources of Pb are contributing to the ambient aerosol. The particle-size profiles for Pb suggest no other source. It was therefore decided that the chemical profiles of the local lead sources were not identical to those listed in the literature. It is possible that variability in lead alloying operations at the secondary lead refinery was causing variability in the profile. This is supported by the excellent fit for Sb and the fact that lead was not included in the original fit.

Two measures of the accuracy of the balance are the number of negative source coefficients and the overall L/S ratio. The balance presented here produced no negative source coefficients and a L/S ratio of 1.4. This ratio is lower than for other CMB studies although the small number of elements fitted here precludes comparison with other work. On the other hand, most of the elements fitted here are elements for which other CMB models show relatively large L/S values. For example, Mizohata and Mamuro /14/ calculated the particle-size distribution of each source component in their overall balance by applying a CMB, using these same sources, to elemental data from each stage of a cascade impactor. They found large values of the observed-to-predicted ratio for both As (5.3) and Sb (3.2). These underpredictions were most evident in the fine particle fraction indicating additional sources of fine particulate not accounted for by the model. Scheff et al /4/, in their study of Chicago aerosol, also realized this problem in concluding that in their mass balance a greater proportion of respirable particulate remained unexplained (50%) than of total particulate (25%). Table 5 shows that, for the present model, there is not a large discrepancy between the L/S ratio for the overall balance on each element and the ratio for balances for each size fraction of each element, thus indicating that the source resolution accounted reasonably well for all fractions of the aerosol. This comparison constituted a third measure of the accuracy of the mass balance. A more accurate knowledge of elemental fractionation between particle sizes from different emission sources would further reduce the difference between the overall balance and the individual particle-size balances.

The L/S values in Table 4, indicate that zinc is the element fitted with the least accuracy. In a traditional CMB, in which there is no consideration of the size distribution of zinc, this underprediction would be accounted for by a larger Zn-rich refuse component as it is in the four-source model. However, consideration of the size distributions of Zn in Figure 2, as well as those of Pb, As and Sb, indicated that there was too much fine particle Zn to be accounted for by the refuse component. Given the existence of a nearby zinc-casting operation, two new size profiles were separated from the zinc particle-size distribution viz. a fine particle Zn vapour-condensation source (Z1) and a medium-sized zinc dust (Z2) source for which profiles are given in Tables 2 and 3. The chemical profile was obtained from zinc melting emissions. /2/ A salt profile was also considered since salt had been used as a road de-icer during three of the sampling periods, all of which had poorly predicted large particle Na concentrations.

Neither the salt nor the zinc profiles could be applied to all samples without causing many negative source coefficients, particularly with the zinc profiles since refuse incineration and the Zn vapour source are similar in Zn concentration and can be regarded as collinear in this data set. However, selective application, where size distributions indicated zinc or salt source contributions, yielded a balance with no negative source coefficients and, as shown in Table 5, a lower L/S ratio of 1.26; lower primarily as a result of the L/S for zinc being reduced from 2.7 to 1.2. The lower overall L/S indicates that including the two additional zinc sources in the model is consistent with the actual sources contributing to the ambient airborne particulate matter.

Increasing the number of elements available for fitting may improve the zinc condensate/refuse incineration separation but also will require consideration of all sources contributing to these additional elements. Work is now underway to examine size distributions for all of the elements determined and to consider other industrial sources of aerosol, such as cement production and steel processing, so that the particle-size CMB can be extended to resolve all of the sources of airborne particulate matter in the study area.

CONCLUSIONS

This study presents a new receptor model, the size-specific elemental mass balance, which can be used to resolve the contributions of aerosol emission sources to different particle-size fractions of the ambient aerosol. Unlike the traditional CMB which utilizes only total elemental concentration, the SSEMB operates on differences in both the chemical composition and the particle-size distribution of emissions from the contributing sources, an approach which was found to be particularly useful where several of these contributing sources have chemically similar emissions, thus confounding the traditional "marker element" approach.

The potential of the new model was demonstrated by determining the contribution to the levels of Pb in the ambient aerosol of automotive exhaust, refuse incineration, soil and lead refinery emissions. The new model does not eliminate all elementally collinear sources but does reduce both the number of such sources and their effect on source apportionment. A more detailed analysis of elemental fractionation amongst particle sizes will be necessary to improve the accuracy of the model.

It was evident that a complimentary coupling of photonuclear and thermal neutron activation analysis, with the accompanying sensitivity, multi-elemental capability and instrumental nature of activation analysis, was essential to the development of the size-specific elemental mass balance.

ACKNOWLEDGEMENTS

The authors would like to express their appreciation to Dr. W.F. Davidson, A. Nowak and Dr. C. Ross of the LINAC facility at the National Research Council, the staff of the University of Toronto SLOWPOKE-II facility and to acknowledge the financial assistance provided by the Ontario Ministry of the Environment and the Natural Sciences and Engineering Research Council of Canada.

REFERENCES

/1/ Gordon, G.E., Environ. Sci. Technol., 14 (1980) 792
/2/ Hopke, P.K., Receptor Modelling in Environmental Chemistry, Wiley-Interscience, New York, (1985)
/3/ Pringle, T.G., and Jervis, R.E., Presented at the International Symposium on Nuclear Analytical Chemistry, Halifax, (1985)
/4/ Scheff, P.A., Wadden, R.A., Allen, R.J., Environ. Sci. Technol., 18 (1984) 923
/5/ Thurston, G.D. and Spengler, J.D., Presented at the 74th Annual Meeting of Air Pollution Control Assoc., New Orleans, (1982)
/6/ Gordon, G.E., Zoller, W.H., Kowalczyk, G.S., and Rheingrover, S.W., Atmospheric Aerosol Source/Air Quality Relationships, American Chemical Society Symposium Series 167, Washington, D.C., (1981) 51
/7/ Pringle, T.G., Landsberger, S., Davidson, W.F., Jervis, R.E., J. Radioanal. Chem. Articles, 90 (1985) 383
/8/ Pringle, T.G., Ph.D. Thesis, University of Toronto
/9/ Kowalczyk, G.S., Gordon, G.E. and Rheingrover, S.W., Environ. Sci. Technol., 16 (1982) 79
/10/ Paciga, J.J., Ph.D. Thesis University of Toronto, (1975)
/11/ Gladney, E.S., Zoller, W.H., Jones, A.G. and Gordon, G.E., Environ. Sci. Technol., 8 (1974) 551
/12/ Alpert, D.J. and Hopke, P.K., Atmos. Environ. 14 (1980) 1137
/13/ Kowalczyk, G.S., Choquette, C.E. and Gordon, G.E., Atmos. Environ., 12 (1978) 1143
/14/ Mizohata, A. and Mamuro, T., Annual Report of the Radiation Center Osaka Prefecture, 20 (1979) 55

Mutagenicity of Complex Mixtures of Polycyclic Aromatic Hydrocarbons in Ambient Air Particulate Matter

by

A.S. Raj and Morris Katz
Centre for Research on Environmental Quality
York University, 4700 Keele Street
North York, Ontario, M3J 1P3

1. Introduction

It has been estimated that 60% or more of the incidence of cancers in man and animals is due to the action of environmental chemicals or pollutants. Polycyclic Aromatic Hydrocarbons (PAH) are a particularly important group of carcinogenic pollutants in addition to many others that are formed through anthropogenic sources. PAH are not carcinogenic per se but may become so after metabolism to reactive products. PAH can be converted to a variety of metabolites. The microsomal mixed-function oxygenases have been implicated in the activation of PAH to toxic, mutagenic, and/or carcinogenic metabolites. These enzymes are multicomponent systems containing several forms of cytochrome P-450, a flavoprotein, NADPH-Cytochrome reductase, P-448 and other endogenous membrane-bound mono-oxygenase systems. Several mechanisms are involved in the alterations of monooxygenase activity by chemicals (Wiebel, 1980), such as the induction of a series of intracellular reactions that cause (1) an increase or decrease of enzymatic activity, (2) interference with catalytic processes, and (3) inactivation or destruction of the cytochrome.

Human exposure to PAH mixtures may produce carcinogenic effects depending on the ratios of the various strong carcinogens to weak- or non-carcinogenic constituents.

2. Materials and Methods

Standard Reference material (SRM) 1649 was purchased from U.S. National Bureau of Standards. SRM 1649 is a mixture of air particulate matter available in the form of dust. Individual PAH have been purchased from Standard Chemical companies.

Mice

Virgin B6C3F1 female mice, 8-9 weeks of age, were used for the *in vivo* bone marrow micronucleus experiments. The mice ranged from 20-22 g in weight and they were fed with Purina Laboratory Rodent Chow and watered ad libitum. The B6C3F1 mouse strain is being used because the mono-oxygenase enzyme system in this strain can be induced by polycyclic aromatic hydrocarbons (Nerbert et al., 1972; Green, 1973).

2.1 Methods

The *in vivo* bone marrow micronucleus assay (Heddle and Salamone, 1981) has been used to test the ambient air particulate matter.

In Vivo Bone Marrow micronucelus Assay

In general, people are exposed to air and particulate matter that could be mutagenic and thus hazardous and a matter of concern. Chromosomal changes comprise a major part of this genetic danger.

The traditional method of examining mitotic chromosomes at metaphase for analysis is tedious and time consuming. Since humans cannot be used in a direct test, a mammalian in vivo test system is very desirable. Therefore, for test purposes bone marrow of common laboratory rodents are an appropriate choice. As an alternative to metaphase scoring, measurement of the micronuclei is appropriate and desirable. Micronuclei are formed in the cytoplasm from fragments of chromosomes left behind at anaphase (because they lack centromeres). Micronuclei persist for some time and so may be scored at interphase. Since most of the cells of a tissue are in interphase there is virtually no time spent finding cells to score (Heddle, 1973).

3. Experimental Results

In the urban air particulate matter of SRM 1649, the following PAH have been identified:

1. Phenanthrene
2. Fluoranthene
3. Pyrene
4. Chrysene
5. Benz(a)anthracene
6. Perylene
7. Benzo(b)fluoranthene
8. Benzo(k)fluoranthene
9. Benzo(a)pyrene
10. Benzo(e)pyrene
11. Benzo(ghi)perylene
12. Dibenz(a,h)anthracene
13. Indeno(1,2,3-cd)pyrene

Carcinogenic and mutagenic potencies of the above PAH have been reported earlier. From the above list they can be broadly classified as:

(i) non-carcinogenic and non-mutagenic (compounds 1, 3)

(ii) slightly carcinogenic and mutagenic (compounds 4, 5, 6)

(iii) more carcinogenic and mutagenic (compounds 7, 9, 12). Based on the above data, and also depending on the structural similarities, we tried to select complex mixtures of mutagenic-mutagenic, mutagenic-non mutagenic and non mutagenic-non mutagenic substances.

3.1 Lethal Dose$_{50}$

A group of 5 mice (both male and female) were treated in each treatment to test the $LD_{50/7}$ of the SRM 1649. The doses of SRM 1649 ranged from 100 mg/kg to 4000 mg/kg.

Air particulate matter of SRM 1649 (in the form of dust) was dissolved in DMSO in appropriate amounts. The mixture was shaken thoroughly in a vortex and the suspension allowed to settle. The supernatant was drawn off and transferred to a separate amber vial. Different dilutions were made and the mice were injected i.p. The mice were checked daily for 7 days for sickness or deaths. The mice used were $B6C3F_1$ females and males. LD_{50} was calculated according to Weil (1952). $LD_{50/7}$ of SRM 1649 was found to be 535 mg/kg.

3.2 Dose Response Studies with SRM 1649

SRM 1649, in the form of dust, was weighed, dissolved in DMSO and allowed to settle. The supernatant was taken and the appropriate dilutions were made.

The doses were adjusted to 250 mg/kg, 500 mg/kg and 1000 mg/kg per body weight of mouse. The mice were injected i.p. with SRM 1649 supernatant. Five mice were used per treatment and samples were collected at 24, 48 and 72 hrs after treatment for testing with the _in vivo_ bone marrow micronucleus assay.

The results indicated that there was no dose-related response of the micronucleated polychromatic erythrocytes (MNPCE). In the 250 mg/kg treatment, on an average, 1.5 MNPCE/1000 PCE at 24 hr, 1.8 MNPCE/1000 PCE at 48 hr, and 1.0 MNPCE/1000 PCE at 72 hr were observed. In the 500 mg/kg treatment, on an average, 1.0 MNPCE/1000 PCE, 1.8 MNPCE/1000 PCE, and 1.0 MNPCE/1000 PCE at 24, 48 and 72 hr respectively were observed. In the 1000 mg/kg treatment, it was observed that 2.8 MNPCE/1000 PCE at 24 hr, 1.6 MNPCE/1000 PCE at 48 hr and 1.0 MNPCE/1000 PCE at 72 hr respectively.

Dose Response Studies with the Reconstituted Mixture of the PAH Present in the Ambient Air Particulate Matter (SRM 1649)

Table 1. Details of the reconstituted mixture of SRM 1649

PAH	Available in SRM 1649 mg/kg	5000 X of the doses available in SRM 1649, adjusted to the weight of mouse and in 0.1 ml DMSO. (g/kg
1. Phenanthrene	4.8±0.3	0.50
2. Fluoranthene	7.4±0.8	0.80
3. Pyrene	6.3±0.4	0.65
4. Chrysene	3.5±0.1	0.35
*5. Benz(a)anthracene	2.5±0.3	0.25
6. Perylene	0.8±0.04	0.08
*7. Benzo(b)fluoranthene	6.2±0.4	0.65
8. Benzo(k)fluoranthene	2.0±0.2	0.20
9. Benzo(a)pyrene	2.6±0.4	0.30
10. Benzo(e)pyrene	----	---
11. Benzo(ghi)perylene	3.9±0.8	0.45
12. Dibenz(a,h)anthracene	0.54±0.04	0.05
*13. Indeno(1,2,3-cd)pyrene	3.4±0.4	0.35

* However, at the time of experiments Benz(a)anthracene, Benzo(b)fluoranthene and Indeno(1,2,3-cd)pyrene could not be included since these PAH were not readily available.

From the stock solution A (5000 X) dilutions B (2500 X) and C (1250 X), were made.

So, the dose response studies were conducted with 1250 X, 2500 X and 5000 X of the mixture of PAH available in the SRM 1649. Following the intra-peritoneal injections, the bone marrow samples were collected to score the micronucleated polychromatic erythrocytes at various sampling times.

The results are tabulated hereunder:

Table 2. Frequency of MNPCE obtained with different doses of reconstituted mixture of SRM 1649

DOSE	* Average no. MNPCE/1000 PCE + S E M Sampling Time (hr)		
	24	48	72
A. 5000 X	2.8±0.7	5.3±1.0	2.3±0.9
B. 2500 X	1.0±0.6	5.0±1.7	4.3±1.0
C. 1250 X	2.0±0.9	11.0±3.1	4.3±1.6

* 5 mice/treatment were used.

From the above results, it is clear that the maximum occurrence of MNPCE (11.0±3.1) were observed at 48h sampling time with the lowest dose of 1250 X.

3.3 Dose Response of Mixture of Mutagens

BaP and DMBA have been chosen to study the dose response in the form of a mixture. Both these mutagens are promutagens. The $LD_{50/7}$ of BaP and DMBA are 232 mg/kg and 84 mg/kg respectively in the mice. Three doses have been chosen to study the dose response of individual mutagens, whereas BaP was kept constant and the doses of DMBA were varied in the mixture. In this study, 1/12, 1/6 and 1/2 of LD_{50} doses have been chosen. Thus, 21 mg/kg, 42 mg/kg and 125 mg/kg for BaP, and 7 mg/kg, 14 mg/kg and 42 mg/kg for DMBA were used. In the case of the mixture 21 mg/kg of BaP was kept constant and the dose of DMBA was varied using 7 mg/kg, 14 mg/kg and 42 mg/kg. From our earlier experience, we know that the peak occurrence of micronucleated polychromatic erythrocytes was at 48 h after the administration of mutagen to the mice. So, in the present experiments the bone marrow samples were collected only at 48 h. The results are tabulated in Tables 3 and 4.

Table 3: Frequency of MNPCE/1000 PCE from bone marrow samples collected at 48 h after the administration of mutagens to mice.

Mutagen	Of LD_{50}	Dose (mg/kg)	MNPCE/1000 PCE ± SEM
BaP	1/12	21	2.0 ± 0.6
	1/6	42	2.4 ± 0.5
	1/2	125	5.2 ± 1.2
DMBA	1/12	7	7.0 ± 1.0
	1/6	14	6.0 ± 0.6
	1/2	42	12.8 ± 2.2
BaP + DMBA	1/12 + 1/12	21+7	1.4 ± 0.4
	1/12 + 1/6	21+14	2.4 ± 0.7
	1/12 + 1/2	21+42	4.4 ± 0.9

Table 4: Data showing the inhibitory effect of promutagens at varying doses.

Mutagens	Dose (mg/kg)	MNPCE/1000PCE (If Additive)	MNPCE/1000PCE (Actual)	Difference	% Inhibition
BaP + DMBA	21+7	2.0+7.0 = 9.0	1.4	7.6	84.4
	21+14	2.0+6.0 = 8.4	2.4	6.0	71.4
	21+42	2.0+12.8=14.8	4.4	10.4	70.3

Similarly, in another set of experiments dose response was studied with 1/4, 1/5 and 1/10 of LD$_{50}$ of BaP, 1/2, 1/4, 1/5 and 1/10 LD$_{50}$ of DMBA. In the mixture BaP was kept constant with 1/10 LD$_{50}$ and the doses of DMBA varied. The results are presented in Tables 5 and 6, which clearly indicate that inhibition occurs when these promutagens are together in the system (Raj and Katz, 1983). Similar results have been reported earlier from our laboratory (Katz and Raj, 1983; Raj and Katz, 1985).

Table 5: Frequency of MNPCE/1000 PCE from bone marrow samples collected at 48 h after the administration of the mutagens in mice.

Mutagen	of LD$_{50}$	Dose (mg/kg)	MNPCE/1000PCE ± SEM
BaP	1/10	25.0	2.6 ± 0.8
	1/5	50.0	4.6 ± 0.08
	1/4	62.5	4.0 ± 1.1
DMBA	1/10	8.4	4.2 ± 0.7
	1/5	16.8	4.6 ± 0.7
	1/4	21.0	4.2 ± 0.8
	1/2	42.0	12.8 ± 2.2
BaP + DMBA	1/10+1/10	25.0+8.4	2.6 ± 0.9
	1/10+1/5	25.0+16.8	3.8 ± 0.7
	1/10+1/4	25.0+21.0	5.0 ± 1.4
	1/10+1/2	25.0+42.0	5.0 ± 1.4

Table 6: Data showing the inhibitory effect of promutagens at varying doses.

Mutagens	Dose (mg/kg)	MNPCE/1000PCE (If Additive)	MNPCE/1000PCE Actual	Difference	% Inhibition
BaP+DMBA	25+8.4	2.6+4.2 =6.8	2.6	4.2	62
	25+16.8	2.6+4.6 =7.2	3.8	3.4	47
	25+21.0	2.6+4.2 =6.8	5.0	1.8	26
	25+42.0	2.6+12.8=15.4	5.0	10.4	68

3.4 Dose Response Studies of Benzo(ghi)perylene in the in vivo Bone Marrow Micronucleus Assay

The LD_{50} of Benzo(ghi)perylene is more than 500 mg/kg in mice. The doses 1/8 of LD_{50} (62.5 mg/kg), 1/4 LD_{50} (125 mg/kg) and 1/2 LD_{50} (250 mg/kg) of Benzo(ghi)perylene were selected in this study. The chemical was dissolved in DMSO and the mice were injected intraperitoneally. Groups of five mice per treatment were used. Bone marrow samples were collected at 24, 48 and 72 hrs after the administration of the chemical. In all the treatments the average number of micronucleated polychromatic erythrocytes per 1000 PCE were less than two which is equivalent to the control background. No dose-related response was observed.

3.5 Dose Response Studies with Benzo(k)fluoranthene

B6C3F1, females, 8 weeks old, were injected i.p. with either 25 mg/kg, 50 mg/kg or 100 mg/kg of Benzo(k)fluoranthene that was dissolved in DMSO. A group of 5 mice were used per each treatment. The bone marrow samples were collected at 24, 48, and 72 hrs after the administration of the chemical. The number of micronucleated polychromatic erythrocytes were scored per 1000 PCE. The results indicated that there was no dose-related response between the amount of mutagen injected and the MNPCE. A maximum number of 3 MNPCE/1000 PCE was observed at 48 hr sampling period in 50 mg/kg treatment.

3.6 Studies on the Effect of Mixtures of PAH, with the in vivo Bone Marrow Micronucleus Assay

The mutagens that were selected for this study included DMBA, BaP, and Benzo(ghi)perylene and their doses were 21 mg/kg, 58 mg/kg and 150 mg/kg respectively. Individual mutagens, a mixture of pairs of mutagens, (DMBA + BaP; DMBA + Benzo(ghi)perylene or BaP + Benzo(ghi)perylene), or a mixture of all the three mutagens were used. A group of 5 mice per treatment were included. Bone marrow samples were collected at 24, 48 and 72 hours after the administration of the mutagens. Micronucleated polychromatic erythrocytes /1000 PCE were scored. The results indicated that there is no spectacular additive effect even when all the three mutagens are included. But, as expected, there was about 65% inhibition in the occurrence of MNPCE from the mice that received a complex mixture of DMBA and BaP. The results are presented in the following Table 7.

Table 7: **Frequency of MNPCE/1000 PCE in the mice that received different mutagens either individually or in mixture**

Mutagens	MNPCE/1000 PCE ± SEM			
	24h	48h	72h	Comments
DMBA	1.6±0.5	8.4±1.4	2.2±0.5	
BaP	2.0±0.8	2.4±0.5	1.2±0.4	
Benzo(ghi)perylene	0.4±0.3	0.8±0.4	2.4±1.0	
DMBA+BaP	2.0±0.8	3.0±0.6	3.2±0.5	About 65% inhibition at 48h compared to DMBA
DMBA+Benzo(ghi)perylene	2.6±0.9	2.4±0.8	2.0±0.7	
BaP+Benzo(ghi)perylene	2.2±0.8	2.4±0.3	1.2±0.7	
DMBA+BaP+Benzo(ghi)perylene	0.75±0.22	2.0±0.9	3.8±0.09	No additive effec

4. Conclusions:

1. $LD_{50/7}$ of standard reference material 1749 was found to be 535 mg/kg when tested in mice.
2. No dose related response was observed either with SRM 1649, or Benzo (k) fluoranthene, or Benzo (ghi) perylene in the *in vivo* bone marrow micronucleus assay.
3. No additive response was observed in the *in vivo* bone marrow nucleus assay when the PAH were tested as complex mixtures, e.g., BaP+DMBA; BaP+DMBA + Benzo (ghi) perylene; BaP + Benzo (ghi) perylene; or DMBA + Benzo (ghi) perylene.

References

1. Green, M.C. (1973) Guideline for genetically determined biochemical variants in the house mouse Mus musculus. Biochem. Genetics, 9,369.

2. Heddle, J.A. (1973) A rapid in vivo test for chromosomal damage. Mutation Res. 18: 187-190.

3. Heddle, J.A. and M.F. Salamone (1981). The micronucleus assay I: In vivo In: Short-term tests for chemical carcinogens, edited by H.F. Stich and R.H.C. San, pp.243-249, Springer-Verlag, New York.

4. Katz, M. and A.S. Raj (1983) Inhibitors of chromosomal breakage in mouse induced by polynuclear aromatic hydrocarbons and other genotoxic agents. Polynuclear Aromatic Hydrocarbons, Eighth Int. Symp. on Mechanisms, Methods and Metabolism (M.W. Cooke and A.J. Dennis, eds.) Batelle Press, Columbus, pp. 697-711.

5. Nebert, D.W., F.M. Gorjon and J.E. Gielen (1972) Aryl hydrocarbon hydroxylase induction by polycyclic hydrocarbons: Simple autosomal dominant trait in the mouse, Nature (London). New Biol., 236,107.

6. Raj, A.S. and M. Katz (1983). Studies on the effect of combination of certain mutagens in the somatic and germ cells of mice using micronucleus assay. XV International Congress of Genetics, New Delhi, India, vol. I: 318. Oxfod and IBH Publishing Co.

7. Raj, A.S. and M. Katz (1985) Studies of inhibition of chromosomal breakage in mouse induced by polynuclear aromatic hydrocarbons and other genotoxic agents. Polynuclear Aromatic Hydrocarbons, Tenth International Symposium (M.W. Cooke and A.J. Dennis, eds.) Battelle Press, Columbus (in press).

8. Weibel, F.J. (1980) Activation and inactivation of carcinogens by microsomal monooxygenases: Modification by benzoflavones and polycyclic aromatic hydrocarbons, in: T.J. Slaga (Ed.). Carcinogenesis vo. 5. Modifiers of chemical carcinogenesis, Raven, New York pp. 57-84.

9. Weil, C. (1952) Tables for convenient calculation of medium effective dose (LD50 or ED50) and instructions in their use. Biometrics, 8: 249-263.

DOSE-RESPONSE STUDIES OF GASEOUS POLLUTANTS ON FOOD CROPS

Jane M. Petitte and D.P. Ormrod
Department of Horticultural Science, University of Guelph
Guelph, Ontario N1G 2W1

ABSTRACT

A long-term dose-response study was conducted in a controlled environment facility using 'Spartan Bonus' carrot plants. Fifteen-day old plants were exposed to either 0, 0.06, 0.12, or 0.18 ul l^{-1} O_3 for seven hours one day each week for a total of 5 weeks. Shoot and root growth analyses were conducted on plants which were harvested one week after each exposure. Leaf area and leaf fresh and dry weights were significantly decreased by the 0.18 treatment after one exposure. Leaf injury was significantly increased by the 0.12 and 0.18 treatments after one exposure. Root fresh and dry weights were significantly decreased in the 0.12 and 0.18 treatments after the third exposure. By the fifth week, significant reductions in leaf and root parameters occurred in the 0.12, as well as the 0.18 treatments. No significant changes were detected in dry matter partitioning between the roots and shoots in any of the treatments.

An experiment was performed, using 14-day old 'New Yorker' tomato plants, to determine changes in plant growth and physiology following exposure to O_3 levels (0, 0.035, 0.070, and 0.105 ul l^{-1}) below those that normally produce visible leaf injury. Leaf and stem growth parameters, stomatal conductance, and chlorophylls a and b were analyzed three days following the seven hour exposure. Neither growth nor chlorophyll was significantly affected by the treatments. Three days after the exposure, stomatal conductance was significantly reduced in all the O_3 treatments.

Research was conducted to determine if comparisons could be made between indoor and outdoor O_3 responses of several crop species. Seeds for indoor experiments of four soybean, two corn, and three wheat cultivars were obtained from the USEPA NCLAN program. These same cultivars had been grown and subjected to O_3 treatments in open-top field chambers in NCLAN studies. In the present experiment, the seedlings were exposed to 0, 0.06, 0.12, or 0.24 ul l^{-1} O_3 for one seven hour period in controlled environment facilities. The results suggested that a good comparison could not be made between indoor and outdoor experiments determining the effect of O_3 using these species.

DOSE-RESPONSE STUDIES OF GASEOUS POLLUTANTS ON FOOD CROPS

Jane M. Petitte and D.P. Ormrod

Department of Horticultural Science, University of Guelph

Guelph, Ontario N1G 2W1

ABSTRACT

A long-term dose-response study was conducted in a controlled environment facility using 'Spartan Bonus' carrot plants. Fifteen-day old plants were exposed to either 0, 0.06, 0.12, or 0.18 $\mu l\ l^{-1}$ O_3 for seven hours one day each week for a total of 5 weeks. Shoot and root growth analyses were conducted on plants which were harvested one week after each exposure. Leaf area and leaf fresh and dry weights were significantly decreased by the 0.18 treatment after one exposure. Leaf injury was significantly increased by the 0.12 and 0.18 treatments after one exposure. Root fresh and dry weights were significantly decreased in the 0.12 and 0.18 treatments after the third exposure. By the fifth week, significant reductions in leaf and root parameters occurred in the 0.12, as well as the 0.18 treatments. No significant changes were detected in dry matter partitioning between the roots and shoots in any of the treatments.

An experiment was performed, using 14-day old 'New Yorker' tomato plants, to determine changes in plant growth and physiology following exposure to O_3 levels (0, 0.035, 0.070, and 0.105 $\mu l\ l^{-1}$) below those that normally produce visible leaf injury. Leaf and stem growth parameters, stomatal conductance, and chlorophylls a and b were analyzed three days following the seven hour exposure. Neither growth

nor chlorophyll was significantly affected by the treatments. Three days after the exposure, stomatal conductance was significantly reduced in all the O_3 treatments.

Research was conducted to determine if comparisons could be made between indoor and outdoor O_3 responses of several crop species. Seeds for indoor experiments of four soybean, two corn, and three wheat cultivars were obtained from the USEPA NCLAN program. These same cultivars had been grown and subjected to O_3 treatments in open-top field chambers in NCLAN studies. In the present experiment, the seedlings were exposed to 0, 0.06, 0.12, or 0.24 $\mu l\ l^{-1}$ O_3 for one seven hour period in controlled environment facilities. The results suggested that a good comparison could not be made between indoor and outdoor experiments determining the effect of O_3 using these species.

INTRODUCTION

Ozone is a common air pollutant present at various times and levels in the commercial crop producing areas of southern Ontario. Past research has indicated that O_3 sensitivity of plants is species as well as cultivar dependent. Some agricultural crops have had more attention than others concerning O_3 sensitivity of growth and yield.

Ozone episodes occur throughout a growing season. Bennett and Oshima (1976) indicated that intermittent six hour exposures of carrot plants to O_3 at 0.19 and 0.25 $\mu l\ l^{-1}$ over a growing season significantly reduced total fresh weight as well as root dry weight at the end of the season. Some of our past studies indicated that leaf growth responses of 16 and 21 day old carrot plants were different when exposed to 0.18 $\mu l\ l^{-1}$ O_3 for one seven hour period (Ormrod and

Petitte, 1985). No data has been reported to show the effects of intermittent low O_3 levels over a growing season. The objective of this experiment was to determine the effects of weekly exposures of carrot plants to the same O_3 levels over a period of five weeks.

Air pollution injury can be classified as either hidden or visible (Heath, 1980). Hidden injury has been defined as biochemical or physiological alterations resulting in decreased plant productivity without visible injury (Heath, 1980). In previous studies (unpublished) using 16-day old tomato seedlings, the results suggested that no significant visible injury occurred on the plants below 0.12 $\mu l\ l^{-1}\ O_3$. However, specific leaf area was significantly reduced at 0.12 $\mu l\ l^{-1}\ O_3$, indicating that the photosynthetic leaf surface area was decreasing faster than leaf dry weight. An experiment was conducted to study hidden injury (growth, stomatal conductance, chlorophyll concentrations) in tomato plants exposed to low levels of O_3.

Experiments to quantify the effects of O_3 on crop growth are needed to permit evaluations of the differences in sensitivity among species, as well as to provide dose-response relationships for the predictions of field effects of O_3 episodes. Previous controlled environment indoor studies and field studies in open-top chambers (Petitte and Ormrod, 1986) have indicated that the sensitivity of a plant to O_3 in the indoor compared to the outdoor environment depends upon species, age, and stresses on the plant. Over the past several years, the United States Environmental Protection Agency's National Crop Loss Assessment Network (NCLAN)(Heck et al., 1984) has conducted field experiments in which cultivars of specific species are exposed to O_3 throughout the growing season. No experiments to test the sensitivity of these same cultivars to indoor O_3 exposures has been reported. The objective of our experiment was to determine if the sensitivity of the young plants would have any relationship to the results obtained in the outdoor experiments.

MATERIALS AND METHODS

Experiment 1

'Spartan Bonus' carrot seeds were planted in Promix BX (1:1:3 mixture of perlite:vermiculite:sphagnum peat moss) soiliess media in white plastic cylindrical containers (200 mm high x 80 mm wide) with five 8 mm holes drilled into the bottom of each to allow for excess water runoff. A one-half strength complete nutrient solution (Hoagland and Arnon, 1950) was supplied daily to the plants. The plants were grown in Conviron Model E8 growth chambers at standard baseline growth conditions (Ormrod et al., 1980). Fourteen days after seeding, 21 plants were placed into each of four continuous stirred tank reactor (CSTR) chambers (Heck et al., 1978; Le Sueur-Brymer and Ormrod, 1984) to allow for approximately an 18 hour acclimation period prior to treatment. The environmental conditions in the CSTR chambers were similar to those described for the growth chamber.

The following day immediately prior to treatment, planar leaf area (PLA) (Ormrod et al., 1983) was measured as a covariate on each plant. One plant was then harvested from each chamber for a 0 day growth point. One of the following O_3 treatments was then imposed upon the plants in one of the four CSTR chambers: 0, 0.06, 0.12, 0.18 $\mu l\ l^{-1}$. Ozone was produced and monitored by a Grace high-voltage generator and a Dasibi (Model 1003-AH) analyzer, respectively. The exposure period continued for seven hours. Following treatment, the plants were placed back into the growth chamber for seven days and then put back into the CSTR chambers. The following day, all plants were rated for leaf injury based upon the percent of visible injury. Four plants from each treatment were then harvested and measurements of leaf area and leaf fresh and dry weights were conducted. Planar leaf area was again measured on the remaining 16 plants in each treatment. Each plant was then exposed for seven hours to the same treatment it had received the previous week. Following exposure, the plants were placed back into the growth chamber for seven days. The same procedure described for the first exposure was continued for a total of five weeks of exposure. Each time all the plants were rated for injury and four plants from each treatment were harvested seven days following the O_3 treatment. From the second exposure onward, both leaf and root measurements were conducted.

The experimental design was a randomized complete block with each block a complete repetition of the experiment. All treatments were replicated three times except for 0.18 $\mu l\ l^{-1}$ which consisted of two replications following the second exposure period. Each treatment in each block was composed of four subsamples. The subsample mean of each block was used in the data analyses. All growth variables were transformed to natural logarithms prior to further analysis. This step was performed in order to normalize the responses and stabilize their variances. Transformation of foliar injury was not required.

The results of the experiment were analyzed using a 3-dimensional response surface model for each growth variable. The covariate, PLA, was used for leaf area and leaf and root fresh and dry weights.

Each response variable was fitted to a second order mutliple regression response surface. The form of the linear model for each response surface used was:

$$Y_i = B_i + \alpha_1(\text{covariate}) + \alpha_2(\text{AGE}) + \alpha_3(O_3) + \alpha_4(\text{AGE})^2$$
$$+ \alpha_5(O_3)^2 + \alpha_6(\text{AGE} \times O_3)$$

where B = blocks.

After the surface was fitted, the interaction coefficient was tested using an F test with a significance level of 0.10. If the AGE x O_3 interaction was not significant, the effects of AGE and O_3 alone were tested by dropping terms out of the model. Contour plots were made of the final models.

Experiment 2

'New Yorker' tomato seeds were planted and cultured in a Conviron Model E8 growth chamber as reported in Ormrod and Petitte (1985). On the 14^{th} day of growth, covariate measurements of plant height, PLA (Ormrod et al., 1983), and plastochron index were made on each plant prior to placement in the CSTR chambers. The environment of the CSTR chambers was similar to that in the growth chamber. One of the following O_3 treatments was then imposed upon the plants in one of the four CSTR chambers for seven hours: 0, 0.035, 0.070, and 0.105 $\mu l\ l^{-1}$. Ozone was generated and monitored as described in Experiment 1. Following treatment, the plants were placed back into the growth chamber. Each morning thereafter about three hours into the photoperiod, stomatal diffusive resistance was measured on the abaxial leaf surface of the first leaf of each plant with a LI-COR 700 transient porometer. On the third day following the exposure, leaf discs of known area were cut from two plants of each treatment, frozen in 80% (w/v) acetone, and kept in the dark for later analysis of chlorophylls a and b (Strain and Svec, 1966). An equal area of leaf discs from the same leaves were dried to base chlorophyll content on leaf dry weight. Post harvest growth measurements included leaf area and leaf and stem fresh and dry weights.

The experimental design was a randomized complete block replicated over time with three blocks. In each treatment, three subsamples were used to determine growth parameters and two subsamples were used in chlorophyll analysis. Stomatal resistance was measured on all the subsamples and converted to stomatal conductance for analysis. The growth variables were transformed to their natural logarithms for analysis of covariance using PLA as the covariate. The mean of the subsamples of each treatment was used in the data analysis.

Experiment 3

Soybeans

Seeds of four soybean cultivars ('Williams-79', 'Amsoy-71', 'Corsoy-79', 'Pella') used in the NCLAN experiments were obtained from Argonne National Laboratory and were planted and cultured in a Conviron Model E8 growth chamber as described by Ormrod and Petitte (1985). Twelve days later the plants were placed into the CSTR chambers for approximately 24 h prior to the O_3 exposure. This allowed for acclimation of the plants to CSTR conditions even though they were similar to those of the growth chamber. Following the acclimation period, plastochron index was measured as a covariate on each plant. One of the following O_3 treatments was then imposed upon the plants in one of the four CSTR chambers for seven hours: 0, 0.035, 0.070, 0.105 $\mu l\ l^{-1}$. Ozone was generated and monitored as described in Experiment 1. The plants were returned to the growth chamber following exposure. Visible injury was determined as described in Experiment 1 three days following exposure immediately prior to the harvest. Leaf area and leaf and stem fresh and dry weights were measured at harvest.

The experimental design was a randomized complete block completely replicated three times over time with four subsamples per treatment per block for 'Corsoy-79' and 'Amsoy-71', and two subsamples per treatment per block for 'Pella' and 'Williams-79'. The means of the subsamples for each treatment of each block were transformed to their natural logarithms, and plastochron index was used as the covariate in the analysis of covariance.

Corn and Wheat

Seeds of two corn ('Pioneer 3780', 'PAG 397') and three wheat ('Roland', 'Abe', 'Arthur') cultivars used in the NCLAN experiments were obtained for Argonne National Laboratory, planted and cultured as described for the soybeans. Ozone exposure was exactly as described for the soybeans, except that the plants were 11 days old. Plant height was measured prior to exposure and used as the covariate in the final analyses. Injury rating and harvesting occurred three days following the exposure. Leaf area and fresh and dry weights were measured for each species. The experimental design and the analysis of covariance were as described for the soybeans. Each treatment of each block consisted of four subsamples.

RESULTS AND DISCUSSION

Experiment 1

Leaf injury in the 0.12 and 0.18 $\mu l\ l^{-1}$ treatments was significantly higher than that in the control carrot plants one week following the seven hour exposure to O_3 (TABLE 1). This observation was made throughout the remainder of the experiment. Injury was not cumulative over the five week period of exposures and appeared to peak and slightly decline after the fourth weekly exposure. After the third exposure, plants in the 0.06 $\mu l\ l^{-1}$ O_3 treatment had some injury, but were not significantly different from the control plants.

Growth was significantly reduced in some of the 0.12 and 0.18 $\mu l\ l^{-1}$ treatments during the experiment (TABLE 1). One week following the first seven hour exposure, the 0.18 $\mu l\ l^{-1}$ O_3 treated plants had significant reductions in leaf area as well as leaf fresh and dry weights. Leaf area was also significantly reduced in the 0.12 $\mu l\ l^{-1}$ treatments.

Following the second exposure, leaf fresh and dry weights were significantly reduced in the two highest O_3 treatments (TABLE 1). No effects were observed in roots or leaf/root dry weight ratio.

Leaf area and leaf fresh and dry weights significantly decreased in the 0.18 $\mu l\ l^{-1}$ treatment following the third weekly exposure (TABLE 1). Root fresh and dry weights were reduced in the 0.12 and 0.18 $\mu l\ l^{-1}$ O_3 treatments.

Even though reductions in growth parameters were observed following the fourth exposure, variation in the data was too great to obtain differences at the $P<0.10$ level of significance (TABLE 1).

Following the fifth week of exposure, significant reductions were observed in all the leaf and root parameters at the 0.12 and 0.18 μl

l^{-1} O_3 treatments (TABLE 1).

No interactive effect of O_3 concentration with the age of the carrot plant at the time of exposure was observed on leaf to root dry weight ratio (TABLE 2). The nonuniform spacing of the contour lines indicated that the response of the partitioning of the dry matter between the leaves and roots decreased as the plant aged (FIGURE 1). The X axis refers to age of the plant at time of exposure to O_3. Plants exposed at 15, 22, 29, 36, or 43 days had 1, 2, 3, 4, or 5 exposures, respectively. The spacing of the contours widened with increasing age because the quadratic component was significant.

Root fresh and dry weights each displayed a complex antagonistic interaction pattern influenced by linear and quadratic responses and a negative significant interaction of age at exposure and O_3 concentration (TABLE 2). If hypothetical lines are drawn across the graph of root fresh weight perpendicular to the Y axis at 0.06, 0.12 and 0.18 μl l^{-1} interpretation of the effects will be facilitated (FIGURE 2). At 0 μl l^{-1} O_3 concentration root fresh weight was at its maximum during the exposure period. A seven hour dose of O_3 at 0.06 μl l^{-1} each week for four weeks did not reduce fresh weight significantly. However, the fifth exposure caused some reduction. At 0.12 μl l^{-1} O_3, the contour lines begin to curve on about day 36. This indicates that in order for the plants at this concentration of O_3 to have the same root weight as the control plants (0 μl l^{-1}), they would have to be about 39 days old. The fifth exposure to O_3 at 0.12 μl l^{-1} significantly reduced root fresh weight when compared to the control plants.

A decrease in root fresh weight was observed in those plants exposed to 0.18 $\mu l\ l^{-1}$ O_3 after the first week of exposure. This reduction due to O_3 and the age of the plant as well as their interaction continued throughout the growing season.

Quadratic dose-response functions represented the effects of age at exposure and O_3 concentration on leaf area (FIGURE 3) and fresh and dry weights (TABLE 2). All the response variables showed significant additive decreases (linear and quadratic effects) from age and O_3 effects. Leaf growth decreased faster in the plants receiving O_3 throughout the season than in those plants receiving no O_3.

The use of response surfaces and contour plots allows one to explain the interaction of O_3 concentration with the age of the plant at exposure. Because O_3 episodes are prevalent throughout a growing season for most crops in populated areas, these results indicate the detrimental interaction of stage of growth with O_3 concentration on carrot root production.

Experiment 2

Stomatal conductances of tomato for the first, second, and third days following exposure to O_3 are recorded in TABLE 3. Conductance was not significantly affected by the O_3 until the third day following exposure when all the O_3 treatments had significant reductions in comparison to the control. Beckerson and Hofstra (1979) reported decreasing stomatal conductances in soybean, cucumber, and radish leaves over five consecutive days (6 h d^{-1}) of exposure to 0.15 $\mu l\ l^{-1}$ O_3. Visible injury did not appear until the last half of the second day of the exposure. The response of stomata on the tomato leaves to a previous O_3 exposure, as observed in the present experiment, indicates the extreme sensitivity of the stomata to low levels of the pollutant.

Neither growth nor chlorophyll a or b was significantly affected by the O_3 treatments. Future studies should allow the plants to grow for several more days following the exposure to determine if stomatal conductances of the O_3 ozone treated plants would recover to the levels of the control plants. Visible injury was not present in any of the treatments.

Experiment 3

-----Soybean

Neither 'Corsoy-79', 'Pella', nor 'Williams-79' soybean plants was significantly affected by the O_3 treatments. 'Amsoy-71', however, did have significant reductions in leaf area and leaf fresh and dry weights at 0.24 $\mu l\ l^{-1}$ O_3 (TABLE 4). Heck et al. (1984) reported the predicted relative yield losses at a seasonal 7 h d^{-1} mean O_3 concentration of 0.09 $\mu l\ l^{-1}$ for 'Corsoy' and two 'Williams' cultivars to be 34.8, 29.1 and 25.9%, respectively. No data were immediately available for either 'Pella' or 'Amsoy' cultivars.

-----Corn

No significant differences were observed between the treated and the control plants. 'PAG 397' and 'Pioneer 3780' cultivars had predicted relative yield losses of 8.1 and 16.7%, respectively, at a seasonal 7 h d^{-1} mean O_3 concentration of 0.09 $\mu l\ l^{-1}$ (Heck et al., 1984).

-----Wheat

Leaf dry weight of 'Abe' wheat plants increased significantly at 0.06 and 0.24 $\mu l\ l^{-1}$ O_3 (TABLE 5), while the leaf dry weight of 'Roland' plants decreased significantly. 'Arthur' wheat plants were unaffected by the O_3. 'Abe', 'Arthur', and 'Roland' cultivars had predicted relative yield losses of 26.7, 27.4, and 45.4%, respectively, at a seasonal 7 h d^{-1} mean O_3 concentration of 0.09 µl l^{-1} (Heck et al., 1984).

-----Summary

The majority of these cultivars did not behave indoors under the stress of one seven hour O_3 exposure as they did outdoors under a seasonal exposure to O_3. The effects of O_3 on early growth was not a good indicator of the effect on final yield. Perhaps an indoor exposure to O_3 may be used as an indication of yield effects in the field if the plants are exposed at a more sensitive stage of development.

LITERATURE CITED

Beckerson, D.W. and G. Hofstra. 1979. Response of leaf diffusive resistance of radish, cucumber and soybean to O_3 and SO_2 singly or in combination. Atmos. Environ. 13:1263-1268.

Bennett, J.P. and R.J. Oshima. 1976. Carrot injury and yield response to ozone. Jour. Amer. Soc. Hort. Sci. 101:638-639.

Heath, R.L. 1980. Initial events in injury to plants by air pollutants. Ann. Rev. Plant Physiol. 31:395-431.

Heck, W.W., R.B. Philbeck, and J.A. Dunning. 1978. A continuous stirred tank reactor (CSTR) system for exposing plants to gaseous air pollutants. Principles, specifications, construction, and operation. ARS, USDA ARS-5-181.

Heck, W.W., W.W. Cure, J.O. Rawlings, L.J. Zaragoza, A.S. Heagle, H.E. Heggestad, R.J. Kohut, L.W. Kress, and P.J. Temple. 1984. Assessing impacts of ozone on agricultural crops: II. Crop yield functions and alternative exposure statistics. Jour. Air Poll. Cont. Assoc. 34:810-817.

Hoagland, D.R. and D.I. Arnon. 1950. The water-culture method for growing plants without soil. Calif. Agric. Exp. Stn. Circ. 347.

Le Sueur-Brymer, N.M. and D.P. Ormrod. 1984. Carbon dioxide exchange rates of fruiting soybean plants exposed to ozone and sulphur dioxide singly or in combination. Can. J. Plant Sci. 64:69-75.

Ormrod, D.P. and J.M. Petitte. 1985. Dose-response studies of gaseous pollutants on vegetable crops. Proceedings Technology Transfer Conference No. 6. I. Air Quality Research. Pp. 263-290.

Ormrod, D.P., D.T. Tingey, and M. Gumpertz. 1983. Covariate measurements for increasing the precision of plant responses to O_3 and SO_2. HortScience 18:896-898.

Ormrod, D.P., P.A. Hammer, D.T. Krizek, T.W. Tibbitts, J.C. McFarlane, and R.W. Langhans. 1980. Base-line growth studies of 'First Lady' marigold in controlled environments. Jour. Amer. Soc. Hort. Sci. 105:632-638.

Petitte, J.M. and D.P. Ormrod. 1986. Indoor and outdoor dose-response studies with cabbage, carrot, and tomato. HortScience 21:786.

Strain, H.H. and W.A. Svec. 1966. Extraction, separation, estimation, and isolation of the chlorophylls. IN: L.P. Vernon and G. R. Seely (eds.). The Chlorophylls. Academic Press, New York. Pp. 21-66.

TABLE 1. Geometric means for response variables. Each response has been adjusted to a common initial size (analysis of covariance).

Response variable	Age of plant at exposure (days)	Ozone concentration ($\mu l\ l^{-1}$)			
		0.00	0.06	0.12	0.18
Leaf area (cm^2)	15	28.30	28.05	21.22*[z]	18.84***
	22	99.29	83.76	74.00	63.82
	29	274.24	293.24	237.94	182.18***
	36	517.50	570.78	449.44	362.85
	43	896.95	791.56	653.93**	521.65***
Leaf fresh weight (g)	15	0.96	1.05	0.83**	0.69**
	22	4.02	3.49	2.85*	2.55*
	29	10.92	12.17	10.09	7.71**
	36	22.76	25.33	19.61	16.44
	43	39.77	35.62	29.93**	25.56**
Leaf dry weight (g)	15	0.120	0.131	0.108	0.091**
	22	0.514	0.440	0.368*	0.330*
	29	1.595	1.742	1.399	1.028***
	36	3.414	3.600	2.872	2.203
	43	6.178	5.463	4.150**	3.347**
Root fresh weight (g)	15	---[y]	---	---	---
	22	0.434	0.465	0.305	0.332
	29	3.387	3.304	2.494**	1.542***
	36	11.439	12.503	9.497	4.958
	43	25.154	28.503	18.430*	13.545**
Root dry weight (g)	15	---	---	---	---
	22	0.041	0.043	0.028	0.029
	29	0.306	0.309	0.231*	0.140***
	36	1.029	1.250	0.959	0.502
	43	2.809	3.099	1.831***	1.250***
Leaf/root dry weight	15	---	---	---	---
	22	14.82	11.26	14.84	10.85
	29	5.99	6.40	7.02	8.89
	36	3.53	3.33	3.60	4.54
	43	2.30	1.98	2.47	2.91
Leaf injury (%)	15	0	0	2***	3***
	22	0	0	6***	11***
	29	0	1	5***	9***
	36	0	2	8***	13***
	43	0	2	5**	6**

---

[z] *, **, *** - significantly different from the control at $P<0.10$, $P<0.05$, $P<0.01$, respectively.

[y] --- roots were not developed enough for accurate collection.

TABLE 2. Equations for fitted response surfaces (final models) and r^2 values.

	r^2
$\mathrm{lnLA} = -0.896 + 0.326(\mathrm{AGE}) - 0.213(O_3) - 0.0034(\mathrm{AGE})^2 - 13.632(O_3)^2$ (FIG. 3)	0.97
$\mathrm{lnLFW} = 2.356 + 0.350(\mathrm{AGE}) + 0.127g(O_3) - 0.0037(\mathrm{AGE})^2 - 14.539(O_3)^2$	0.97
$\mathrm{lnLDW} = 0.208 + 0.357(\mathrm{AGE}) - 0.102(O_3) - 0.0037(\mathrm{AGE})^2 - 14.084(O_3)^2$	0.97
$\mathrm{lnRFW} = -9.253 + 0.482(\mathrm{AGE}) + 8.242(O_3) - 0.0043(\mathrm{AGE})^2 - 36.856(O_3)^2 - 0.168(\mathrm{AGE} \times O_3)$ (FIG. 2)	0.96
$\mathrm{lnRDW} = -4.565 + 0.474(\mathrm{AGE}) + 5.084(O_3) - 0.0041(\mathrm{AGE})^2 - 27.850(O_3)^2 - 0.140(\mathrm{AGE} \times O_3)$	0.97
$\mathrm{lnLFRTDW} = 37.620 - 1.502(\mathrm{AGE}) + 0.015(\mathrm{AGE})^2$ (FIG. 1)	0.91

TABLE 3. Stomatal conductances (cm s^{-1}) of the abaxial surface of the first primary leaf of 'New Yorker' tomato seedlings; 1, 2, and 3 days following a 7 hour exposure to O_3.

	Ozone concentration ($\mu l\ l^{-1}$)			
Day after exposure	0.00	0.035	0.07	0.105
1	0.47	0.55	0.47	0.53
2	0.64	0.56	0.53	0.62
3	0.52	0.45**^{z}	0.45**	0.45**

^{z} ** - significantly different from the control at $P<0.05$.

TABLE 4. Effects of a 7 hour O_3 exposure on soybean 'Amsoy-79' leaf and stem growth.

	Ozone concentration ($\mu l\ l^{-1}$)			
Growth variable	0.00	0.06	0.12	0.24
Leaf area (cm^2)	114	110	114	101**[z]
Leaf fresh weight (g)	2.71	2.66	2.75	2.47*
Leaf dry weight (g)	0.448	0.425	0.429	0.415
Stem fresh weight (g)	0.653	0.640	0.669	0.610
Stem dry weight (g)	0.076	0.076	0.079	0.074

[z]*, ** - significantly different from the control at $P<0.10$, $P<0.05$, respectively.

TABLE 5. Effects of a 7 hour O_3 exposure on the leaf growth of three wheat cultivars.

	Ozone concentration ($\mu l\ l^{-1}$)			
Growth variable	0.00	0.06	0.12	0.24
Leaf area (cm^2)				
Abe	17.46	18.92	18.17	19.69
Arthur	15.10	14.97	15.88	15.35
Roland	15.33	14.44	16.28	13.87
Leaf fresh weight (g)				
Abe	0.487	0.544	0.482	0.538
Arthur	0.447	0.445	0.446	0.425
Roland	0.463	0.423	0.492	0.432
Leaf dry weight (g)				
Abe	0.090	0.102*	0.091	0.105**
Arthur	0.086	0.084	0.083	0.082
Roland	0.093	0.079***	0.089	0.083**

[z] *, **, *** - significantly different from the control at $P<0.10$, $P<0.05$, $P<0.01$, respectively.

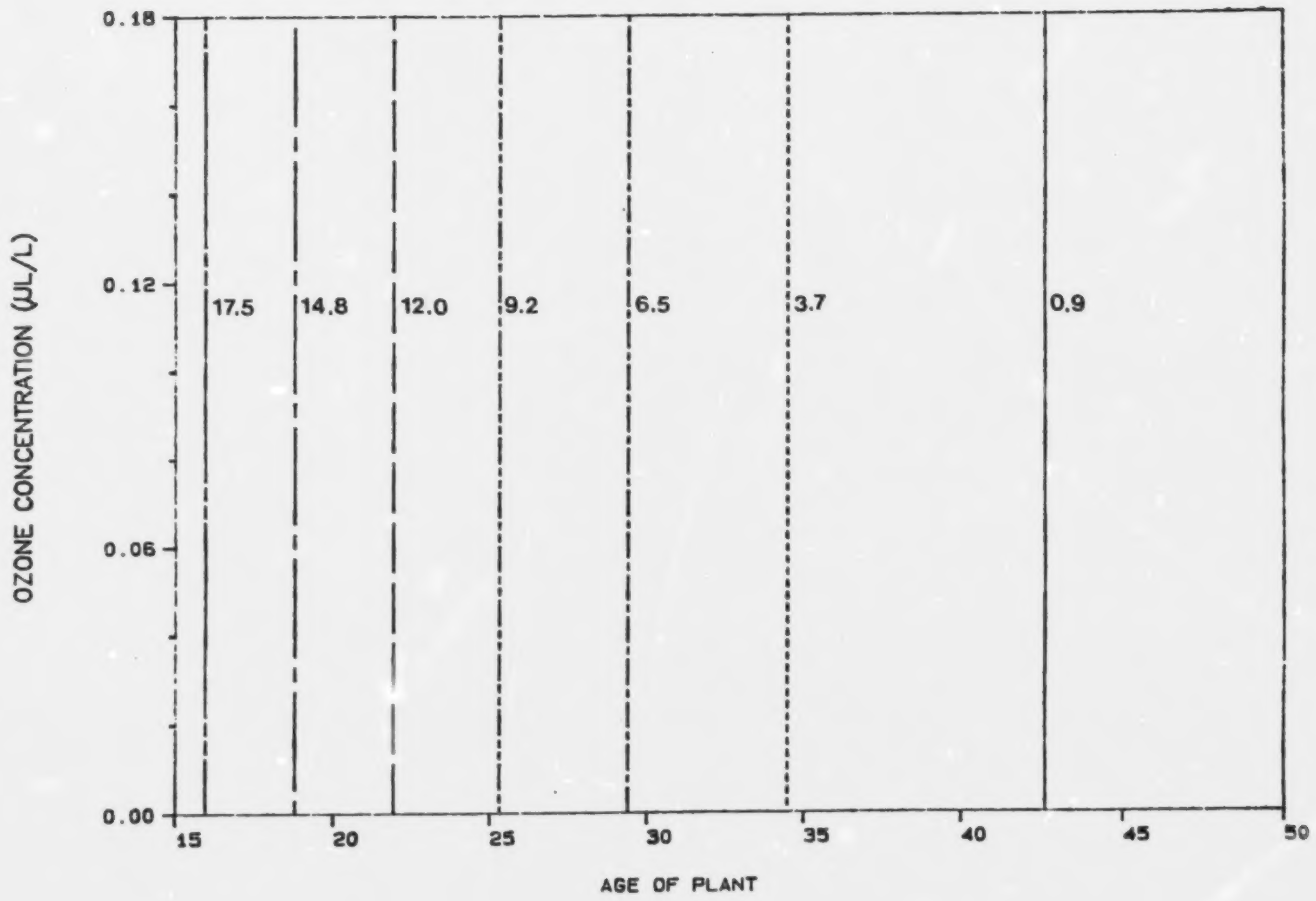


FIGURE 1. Contour plot illustrating the response of carrot leaf/root dry weight to weekly O_3 exposures throughout a growing season. The numbers on the contour lines indicate the fitted value for the line.

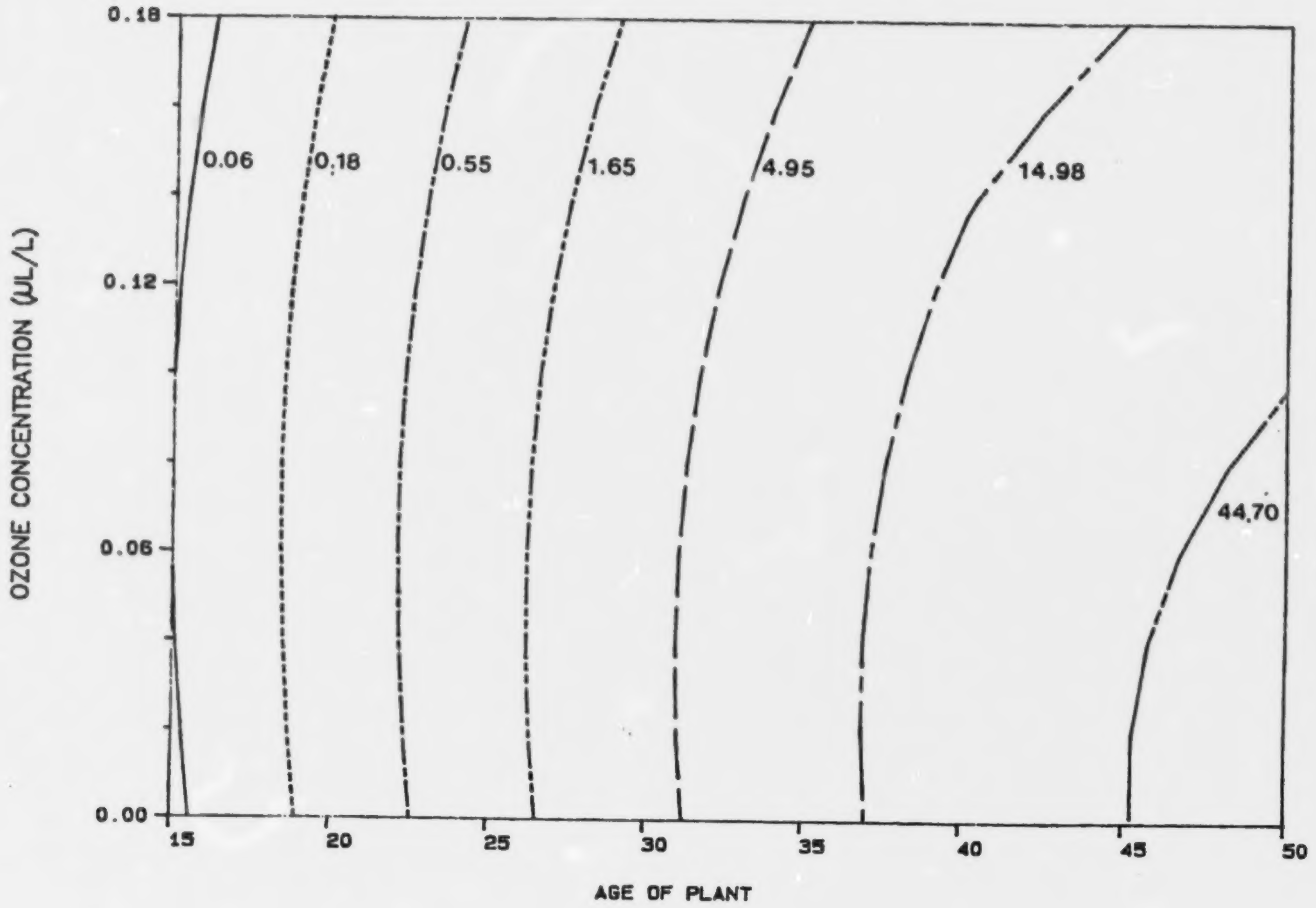


FIGURE 2. Contour plot illustrating the response of carrot root fresh weight to weekly O_3 exposures throughout a growing season. The numbers on the contour lines indicate the fitted value for the line.

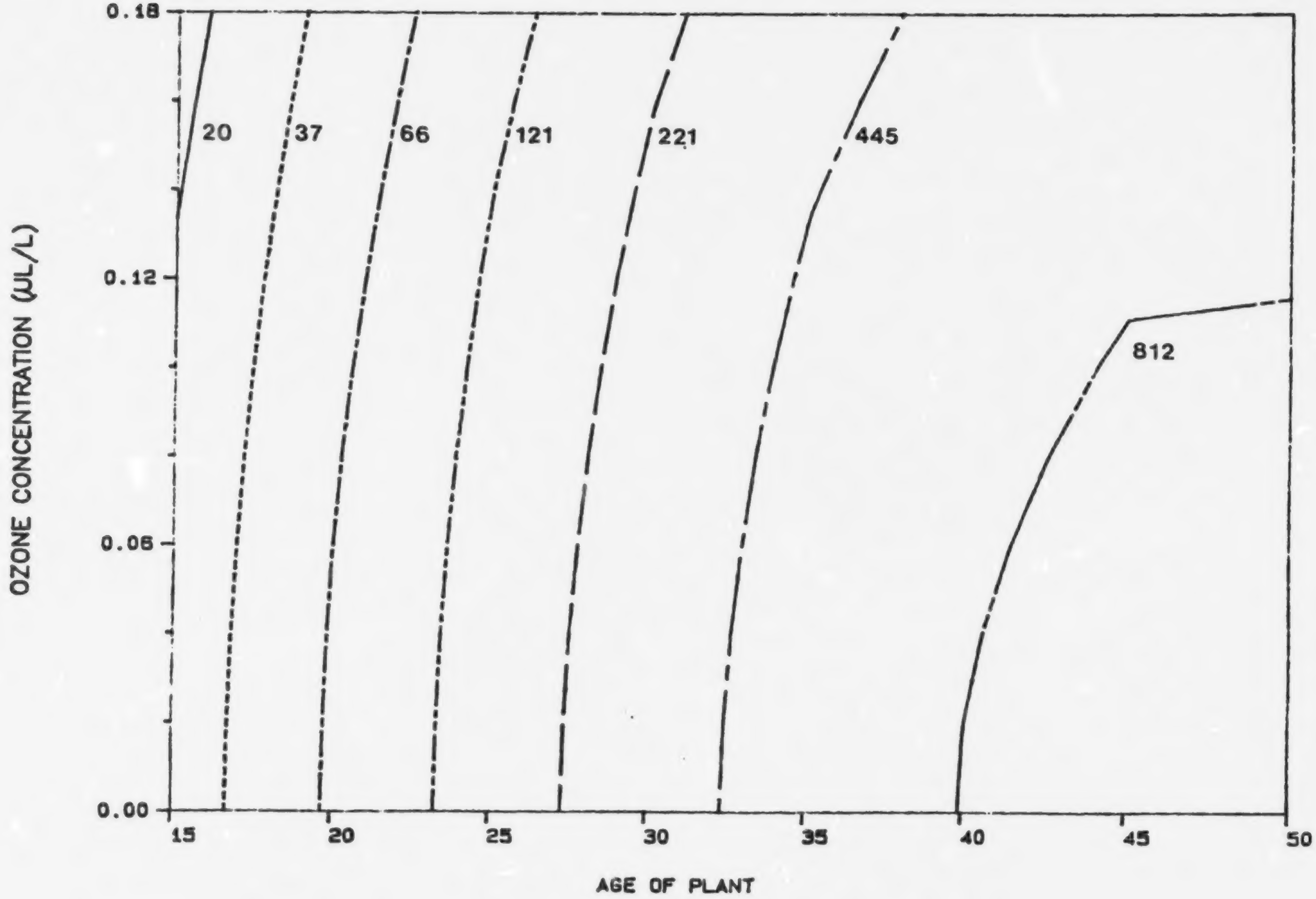


FIGURE 3. Contour plot illustrating the response of carrot leaf area to weekly O_3 exposures throughout a growing season. The numbers on the contour lines indicate the fitted value for the line.

Selection of Ozone Insensitive White Bean Varieties Using Digitized Video Image Analysis

T. E. Michaels
Department of Crop Science
University of Guelph

Abstract

Previous experiments using visual estimates of damaged leaf area following exposure of common bean (Phaseolus vulgaris L.) plants to ozone in growth chambers indicated that experienced evaluators are important in insuring rapid and consistent estimation of ozone damage. The objective of this study was to evaluate an alternative evaluation system that could be used by inexperienced technicians. A digitized video image analysis (DVIA) system was developed that evaluated the pixel brightness of video images of ozone--exposed bean leaves, and determined the mean and standard deviation of the resulting pixel brightness distributions for each leaf. Thirty-five near homozygous breeding lines were produced from crosses between the licensed white bean cultivars 'Seafarer', 'Kentwood' and 'Ex Rico 23', and ozone insensitive cultivars 'Gold Crop', 'French Horticultural Bean' and 'Midnight'. Fourteen-day-old seedlings of the 35 breeding lines and parental cultivars were exposed to 0.20 ppm ozone for 6 hours during each of 4 days in growth chambers. On day 5, injury of the two unifoliate leaves was evaluated using the visual Horsfall-Barratt scale and the DVIA system. The standard deviation of pixel brightness values was in good agreement with the damaged leaf area estimates (r=0.68). Cluster analysis of the standard deviation data placed 29 of 41 entries in the same sensitivity group as those based on visual estimates of damaged leaf area. Improvement in ozone insensitivity was most noticeable for breeding lines derived from the early white bean cultivars 'Seafarer' and 'Kentwood'.

Introduction

White bean, also called navy or pea bean, is the predominant common bean (Phaseolus vulgaris L.) type grown in Ontario. About 40,000 hectares of white beans are cultivated annually in southwestern counties of the Province, and generate a farmgate income of approximately $40 million. The currently licensed and recommended white bean varieties are susceptible to leaf damage following episodes of high atmospheric ozone concentration during the growing season. Ozone-induced leaf damage, or bronzing, has been estimated to reduce white bean yields by more than 30% (Hofstra et al., 1978). A 1984 report by the Ontario Ministry of the Environment cited white beans as suffering a higher percentage loss from ozone than other crops studied: a 12% loss in region 5 and 7% loss in region 4 (Linzon et al., 1984). The monetary value of these losses was estimated at up to $1,185,000. Because of this culture's reliance on fossil fuels, it seems unlikely that ozone levels will decline in the short term.

During the development of new white bean cultivars for commercial use, thousands of genetically different plants are generated, and those with the best combinations of the desired agronomic and quality attributes are selected. In our breeding program, ozone damage has routinely been evaluated by estimating the percentage of seedling leaf area damaged by exposure to ozone in growth chambers using the Horsfall-Barratt scale. In this 12 division scale, divisions representing damaged leaf areas near 50%, where the eye's acuity is lower, cover a wider range of disease severity than divisions representing damaged leaf areas near 0 or 100%. (Horsfall and Barratt, 1945). Our experiences with the Horsfall-Barratt scale indicate that well trained evaluators are important in insuring rapid and consistent estimation of ozone damage. In addition, aprolonged evaluation session can cause fatigue in the evaluator which results in decreased speed and accuracy.

Video image analysis offers an alternative electronic method of assessing plant disease severity. In this technique, a video camera transmits the image of a leaf to a video digitizing circuit board installed in a microcomputer. The video board divides the image into 60000 pixels, assesses the brightness of each pixel, and assigns each a brightness value ranging from 0 (black) to 255 (white). In previous video image analysis systems, the ratio of pixels with brightness values representing diseased leaf tissue to the total number of pixels corresponding to healthy and diseased leaf tissue was used to compute the percentage of damaged leaf area (Lindow, 1983). Successful operation of the video image analysis system required distinct differences in brightness among healthy plant tissue, diseased tissue, and background. In preliminary attempts at digitized video image analysis of ozone damaged leaves, I had little success at obtaining distinct brightness differences between damaged and healthy leaf tissue. I observed, however, that the frequency distribution of pixel brightness from healthy leaves differed from those of ozone-damaged leaves. Healthy leaves tended to produce frequency distributions with smaller standard deviations than the distributions from ozone damaged leaves. The mean brightness of ozone-damaged leaves also appeared to be somewhat higher or lower than the mean brightness of healthy leaves.

Our goal was to develop an alternative means of evaluating ozone damage induced in a large number of white bean breeding lines that did not require experienced operators or induce fatigue, yet was rapid and accurately assessed genotypic differences in ozone insensitivity. The objective of this study was to determine whether the mean and standard deviation of the frequency distribution of pixel brightness from video images of ozone-exposed common bean leaves could be used to identify ozone insensitive breeding lines.

Materials and Methods

Thirty-five white bean breeding lines were developed from crosses between the ozone insensitive common bean cultivars 'French Horticultural Bean', 'Midnight' and 'Gold Crop' and ozone sensitive white bean cultivars 'Seafarer', 'Ex Rico 23' and 'Kentwood', followed by selection for plant and seed type in the F_5 and F_6 generations. Two Fourteen-day-old seedlings at the unifoliate stage of these thirty-five lines and the six parental cultivars were screened for ozone sensitivity in each of four growth chambers in Spring, 1986. One of the chambers received no ozone while the others received 0.20 ppm ozone for 6 hours during each of 4 consecutive days. On day 5, injury of the two unifoliate leaves of each plant was rated using the Horsfall-Barratt scale and the Digitized Video Image Analysis system. Only the Digitized Video Image Analysis system was used to rate the plants from the chamber receiving no ozone. Prior to digitization, the leaves were detached from the plant and placed on a black velvet background with illumination from a small fluorescent desk lamp. The DVIA system used a Panasonic WV 1330 video camera interfaced with a Techmar Video Van Gough expansion board installed in an IBM Portable PC. User-written software computed the frequency of pixels with each brightness value, and determined the mean and standard deviation of the pixel brightness distribution for each leaf image. The difference in mean and standard deviation between ozone exposed and unexposed leaves of the same genotype was also computed. Horsfall-Barratt scores and video image data were evaluated using an Analysis of Variance. Log transformations of the Horsfall-Barratt and standard deviation data were required to meet the assumptions of the Analysis of Variance. Where significant differences existed, entry means were separated based on a K-means cluster analysis where means were separated into four groups.

Results

Analysis of variance of the Horsfall-Barratt scores of damaged leaf area and the pixel brightness distribution statistics indicated that breeding line differences were significant. Damaged leaf area was most closely correlated with the standard deviation of the pixel brightness distribution (Table 1). Damaged leaf area was not, however, correlated with the mean of the brightness distribution. Differences between exposed and unexposed leaves as measured by the brightness distribution statistics were not more closely associated with estimated damaged leaf area than standard deviation of the exposed leaves alone.

Of the parental white bean cultivars, 'Seafarer' was grouped with the most ozone-sensitive breeding lines, 'Kentwood' was placed in an intermediate group, and 'Ex Rico 23' was placed in the least sensitive group (Table 2). Two of the common bean parents used as donors of ozone insensitivity, 'Midnight' and 'French Horticultural Bean', were also grouped with the least sensitive group. However, the supposedly ozone-insensitive parent 'Gold Crop' was placed with breeding lines of intermediate sensitivity.

Twenty-two breeding lines were less ozone sensitive than their white bean parent. Six were more sensitive, and seven were placed in the same group as their white bean parent. Improvement was most noticeable for breeding lines derived from the early white bean cultivars 'Seafarer' and 'Kentwood'. Five lines derived from 'Ex Rico 23' maintained the low sensitivity of the parent line. Cluster analysis of the standard deviation data placed 29 of 41 entries in the same sensitivity group as those based on visual estimates of damaged leaf area.

Discussion

The standard deviation of the pixel brightness distribution of ozone-exposed leaves was an acceptable indicator of ozone sensitivity of the various breeding lines. Standard deviation was highly correlated with visual estimates of damaged leaf area. The lack of perfect correlation between damaged leaf area and standard deviation did not necessarily reflect flaws in the DIVA system, since the damaged leaf area was estimated visually, and was itself subject to error. Low standard deviations indicated ozone insensitivity, while high standard deviations indicated greater sensitivity. Leaves from ozone insensitive plants had a uniformly green color, which produced a distribution with a high number of pixels in a small range of brightness values. Damaged leaves displayed several different symptoms including chlorosis, necrosis and bronze stippling in addition to healthy green tissue, which resulted in distributions with pixel brightness values spread over a wider range. Increased tissue damage did not substantially alter the mean of the brightness distribution, probably because some symptoms such as chlorosis produced brighter pixels upon digitization than healthy green tissue, while other symptoms such as necrosis caused darker pixels.

A comparison of leaf brightness distributions of exposed and unexposed leaves did not improve the ability of the system to distinguish differences among the breeding lines since the leaves of genotypes used in this study showed little variation in their brightness distributions prior to ozone exposure.

The visual and DVIA systems could potentially differ in how the chlorotic, necrotic and bronzing symptoms are interpreted. Three leaves with equal areas of damage, but each differing in the primary symptom should be ranked equally by an experienced evaluator using the visual method, but may be ranked differently by the DIVA system since the brightness of the symptoms differ. Because plants selected based on this ozone sensitivity screen would be those with no damage symptoms, this difference in evaluation would not be important in a breeding program. However, in experiments quantifying the genetic variation for ozone insensitivity, the difference in interpretation could cause differences in heritability estimates. In cases of extremely severe ozone damage where the symptom is uniform across the leaf, the resulting standard deviation would be low, and the leaf rated as insensitive. In this case, a rating formed from a combination of standard deviation and mean might be useful.

The primary advantage of this digitized video analysis system is its ease of use by inexperienced personnel, and the consistency of the evaluations regardless of the duration of the evaluation session. In a preliminary study, an inexperienced technician successfully collected brightness data on leaves after a 30 minute training session. Data collection using the video system took approximately as much time as the visual analysis. Each leaf was digitized and saved to a file in approximately 15 seconds. Positioning the leaf on the background and entering an identification code into the computer required more time than the digitizing and file manipulation steps.

The system may have applications to field studies where a portable video tape recorder is used to collect the images of the tissues to be evaluated.

References

Hofstra, G., D. A. Littlejohns and R. T. Wukasch. 1978. The efficacy of the antioxidant ethylene diurea (EDU) compared to carboxin and benomyl in reducing yield losses from ozone in navy bean. Plant Dis. Rep. 62:350-352.

Horsfall, J. G. and R. W. Barratt. 1945. An improved grading system for measuring plant diseases. (Abstr.) Phytopathology 35:655.

Lindow, S. E. 1983. Estimating disease severity of single plants. Phytopathology 73:1576-1581.

Linzon, S. N., R. G. Pearson, J. A. Donnan and F. N. Durham. 1984. Ozone effects on crops in Ontario and related monetary values. Ontario MOE ARB-13-84-Phyto.

Table 1. Correlations among visual ratings and digitized video image pixel brightness distribution statistics.

	Mean	Δ mean	Standard deviation	Δ Standard deviation
Damaged leaf area	0.19	0.21	0.68	0.65
Mean		0.65	0.16	0.10
Δ mean			0.15	0.24
Standard deviation				0.93

Table 2. Mean damaged leaf area based on visual observations, and mean and standard deviation of digitized video image pixel brightness distributions.

Breeding line	Pedigree	Damaged leaf area	Pixel brightness	
			Mean	Standard deviation
		%		
19	F[†] x S	1.2 a[‡]	138.5 c	26.5 a
9	E x G	2.0 a	131.4 a	31.1 b
11	F x S	2.3 a	139.9 c	27.0 a
30	(E x G) x M	2.3 a	132.4 a	25.4 a
1	S x G	2.9 a	133.8 b	27.2 a
3	S x G	2.9 a	136.0 b	26.4 a
6	K x G	2.9 a	136.1 b	26.8 a
12	F x S	2.9 a	137.2 b	26.0 a
14	F x S	3.1 a	139.2 c	27.8 a
27	(K x F) x M	3.7 a	133.2 a	29 0 a
	Midnight	4.5 a	128.1 a	26.7 a
28	(E x G) x M	4.7 a	142.1 c	28.6 a
	Ex Rico 23	5.1 a	136.8 b	26.4 a
20	F x S	5.3 a	132.1 a	28.1 a
21	S x G	5.9 a	148.5 d	31.7 b
8	E x G	6.3 a	136.1 b	27.3 a
4	S x G	6.4 a	136.9 b	27.4 a
31	(E x G) x M	6.8 a	135.4 b	25.9 a
5	K x G	7.4 a	143.2 c	28.0 a
24	K x F	8.0 a	133.7 b	27.8 a
15	F x S	8.4 a	137.4 b	28.8 a
22	S x G	8.5 a	142.5 c	27.1 a
23	S x G	8.6 a	135.6 b	30.7 b
	French Horticultural	8.8 a	129.5 a	27.1 a
13	F x S	9.5 a	137.8 b	27.7 a
17	F x S	10.1 a	137.6 b	27.4 a
7	K x G	12.0 a	130.8 a	30.5 b
10	E x G	13.8 b	137.6 b	28.1 a
	Kentwood	15.6 b	138.3 c	31.7 b
2	S x G	17.2 b	138.9 c	27.1 a
29	(E x G) x M	18.0 b	148.4 d	28.8 a
25	K x F	18.9 b	147.5 d	31.8 b
18	F x S	19.7 b	142.0 c	30.0 b
26	(K x F) x M	22.1 b	133.8 b	33.2 c
16	F x S	24.9 b	140.1 c	28.6 a
	Gold Crop	27.7 c	134.3 b	33.9 c
34	G x E	33.7 c	140.0 c	32.5 b
33	(G x E) x M	34.0 c	138.0 b	35.3 c
35	K x F	35.1 c	141.9 c	30.6 b
	Seafarer	53.3 d	135.7 b	34.0 c
32	(K x F) x M	60.0 d	135.2 b	40.9 d

[†] F = French Horticultural Bean, S = Seafarer, E = Ex Rico 23, G = Gold Crop, M = Midnight, K = Kentwood

[‡] groups established by k-means cluster analysis

Nickel Carbonyl Ambient Monitor

D.R. Hastie and H.I. Schiff

Chemistry Department
York University
4700 Keele St.
Downsview, Ontario
M3J 1P3

Nickel Carbonyl Ambient Monitor

Introduction

The purpose of the contract was to produce an instrument capable of measuring ambient levels of Nickel Carbonyl down to the Ontario Provincial standard of 0.5 μgm^{-3} (70 ppt).

The analytical technique that was chosen uses the chemiluminescence which results when Nickel Carbonyl is reacted with ozone.

General Theory of Operation

The gas-phase reaction of Nickel Carbonyl ($Ni(CO)_4$) and ozone (O_3) in the present of carbon monoxide (CO) produces a characteristic luminescence with an intensity linearly proportional to the concentration of Nickel Carbonyl. Specifically,

$$Ni(CO)_4 + O_3 \qquad NiO + \text{products}$$

$$NiO + CO \qquad Ni + CO_2$$

$$Ni + O_3 \qquad NiO^* + O_2$$

Light emission results when electronically excited NiO molecules decay to lower energy states.

The ambient air sample enters the instrument through a single flow control capillary. The sample is then mixed with carbon monoxide and ozone and admitted to the reaction chamber where the chemiluminescence is measured. An output signal is continuously generated which records the level measured.

Instrument Modification

The Thermoelectron Corporation (TECO) markets a Nickel Carbonyl monitor, model 14N, but the specifications indicate it is not sufficiently sensitive for Ministry requirements. The detection limit is listed as $0.7\mu gm^{-3}$(.1ppb) Thus for this contract this instrument would have needed to be modified. The Nickel Carbonyl instrument is a modified model 14B/E NO/NO_x instrument. Since modifications would have been required to the Nickel Carbonyl instrument, it was decided it would be more cost effective to purchase the NO/NO_x instrument and modify it to measure Nickel Carbonyl at the required sensitivity.

The following modifications were made to the commercial NO/NO_x instrument:

a) The volume of the reaction vessel was increased from 10 to 100 cubic centimeters. This increases the number of Nickel atoms being viewed by the photomulitplier and thus increases the sensitivity.

b) The air flow through the system was increased which increases the number of Nickel atoms passing through the cell and thus the sensitivity.

c) The red filter in front of the photomultiplier was replaced with an Andover 023FG11-50 blue filter. This was selected to maximize transmission of the NiO^* chemiluminescence while rejecting the NO_2^* chemiluminescence from NO and the FeO^* chemiluminescence from $Fe(CO)_5$. In this way the selectivity toward $Ni(CO)_4$ was assured.

d) An additional plumbing line to allow addition of CO was included. It was found necessary to include a needle value on this line to optimize instrument sensitivity. A scrubber containing iodine and activated charcoal was included on this line to remove any carbonyl in the carbon monoxide cylinder. (In the course of this work it was found that normal CP grade carbon monoxide contains extremely variable amounts of carbonyls. We recommend a high purity grade of CO in an aluminum cylinder be used for this instrument.)

e) The sample and hold electronics of 14 B/E is now redundant and has been bypassed. The signal from the photomultiplier now passes through an amplifier, a temperature compensation board, and switch is then filtered and appears as the recorder output. None of the original control electronics is used.

f) While running instrument tests the photomultiplier tube envelope fractured. Thus we had to replace this tube. A direct replacement was quoted as being $3,000. The high cost is related to the low quantum efficiency of photomultipliers in the red end of the spectrum. However, for this instrument we block the red end of the spectrum. As a result a cheaper photomultiplier could be used. We purchased a Hamamatsu Model R329 tube for $300 U.S. which could be used without modifying the instrument. In addition this tube has a far lower dark current at room temperature and while it was higher than the cooled tube the improvement was so small we decided to disconnect the thermoelectric cooler.

g) The final modification to the instrument was to replace the supplied pump with a rotary vacuum pump. It by found that using the diaphram pump that the relationship between signal and Nickel Carbonyl concentration was not linear. It was found that by lowering the cell pressure linearity was achieved. This necessitated the replacement of the diaphram pump with a rotary vacuum pump. It should be noted here that ozone reacts with rotary pump oil in making it very thick and potentially capable of seizing the pump.

Two precautions need to be taken to lengthen the life of the pump. Firstly the TECO ozone destruction catalyst should be placed between the instrument and the pump, not after the pump as with the 14B/E. Secondly the pump oil should be replaced regularly.

Instrument Tests

Before delivering the instrument many tests were performed to ensure it met the contract standards. The two instrument parameters that were of most concern were sensitivity (and its associated parameter, detection limit) and linearity. We also examined some parameters related to the reliability of the instrument. The bulk of the tests however related to the development of a calibration and sampling protocol.

Instrument Linearity

This section of the work was expected to be relatively straighforward. The mechanism for this reaction is well known and predicts a linear relationship between signal and Nickel Carbonyl concentration. Varying parameters such as air flow, ozone flow and reaction cell pressure would be expected to change the sensitivity (the signal per unit of concentration) but a linear relationship would be expected for any parameter combination. (This is not strictly true for low ozone concentrations but this case is never encountered so was not considered)

Figure I shows the linearity check run for an early geometry and using the TECO supplied pump. Non linearity is clear. For a halving of the Nickel Carbonyl concentration the signal drops by a factor of just over 2 whereas halving the concentration again drops the signal by an order of magnitude.

We found both the signal magnitude to increase and the signal concentration relation to more closely approach linearity as the air ozone and the carbon monoxide were premixed closer to the reaction vessel. The prereactor in particular showed some irreproducible behaviour and since it appeared not to be necessary for NO signal rejection it was removed. We tried many combinations of flows and plumbing schemes but it was not until we lowered the reaction vessel pressure that linear behaviour became reproducible. Figure II shows the same plot as Figure I but for the final system geometry and shows the instrument has a linear relationship between signal and Nickel Carbonyl concentration.

Note:

It is important to understand how the linearity tests were performed. A constant ambient air flow was doped with varying flows from the Nickel Carbonyl cylinder. We used Hastings mass flowmeter for the flow measurements but found that the heat of the flowmeter was sufficient to decompose the $Ni(CO)_4$. Thus the protocol was to set the Nickel Carbonyl flow and measure it using the flowmeter. The signal on the instrument was zero at this time. We then turned the flowmeter off and as it cooled the signal rose. After 15 minutes the signal stabilized and this value was used. The flowmeter was turned on again to ensure the flow had not changed. This procedure was followed for all flows, i.e. for all concentrations.

Sensitivity and Detection Limit

Once linearity was assured it was then possible to determine the sensitivity and detection limit. Using the scale remaining from the NO/NO_x application we found the sensitivity to be 4 concentration units for 1 ppb of Nickel Carbonyl. This gives a sensitivity of 4 concentration units per ppb. The peak to peak noise on the background is 0.02 concentration units corresponding to <10 ppt of Nickel Carbonyl. Thus using the instrument with a chart recorder output the detection limit is 10 ppt and could be improved using signal averaging.

Calibration Sources

a) Permeation Source.

The initial attempt at an in situ calibration source was a permeation device. In this case Nickel Carbonyl in a container at 35^{O}C was separated from the air stream going to the instrument by a wafer of teflon. The concentration gradient across the wafer then drives diffusion, or permeation, of Nickel Carbonyl through the wafer. A constant mass of Nickel Carbonyl would pass through the wafer which could be fed to the instrument for calibration. We used wafer as low as .010" thick but were unable to get sufficiently high permeation rates for a sensible calibration source.

Diffusion Source

The diffusion source is similar in principle to the permeation source except that the wafer is replaced by a short length of capillary tubing. This worked much better than the permeation source but was found to be more variable than could be tolerated. On opening the source we found nickel deposits on many occasions showing Nickel Carbonyl decomposition in the capillary which changes the geometry and thus the diffusion rate. The diffusion device also showed variable rates when the unit was moved showing the effects, we believe, of Nickel Carbonyl being splashed within the device.

Calibration cylinders

At the beginning of this project we attempted to find a supplier of gas cylinders of Nickel Carbonyl at part per million mixtures. We were successful but believed they were overly expensive and since we expected the permeation device to work we did not pursue the option.

The failure of permeation and diffusion devices left us with only the cylinder as an option. The long lead time and cost of the commerical product led us to make our own cylinders. We had a passivated aluminum cylinder pressure tested and a new valve fitted. In this we made mixtures of Nickel Carbonyl in Nitrogen by pumping the cylinder to 10^{-5} Torr, adding 10's of Torr of $Ni(CO)_4$ and filling the cylinder to over 1000 psi with nitrogen. We then calibrated these cylinders regularly. We have seen substantial decay of the standard. We feel this is largely due to decomposition within the cylinder. This could be improved by making the mixture in carbon monoxide rather than nitrogen, a procedure which is done by the commerical supplier but which we were reluctant to do.

We thus recommend the purchase of standard Nickel Carbonyl standards in carbon monoxide but in light of our experience we recommend regular calibrations until confidence in the stability of the standard is established.

Calibration of Nickel Carbonyl Tanks

To determine the concentration of Nickel Carbonyl in cylinders an independent absolute analysis system was developed. The principle is to take on some of the gas mixture and collect the Nickel Carbonyl in a solution. The nickel is oxidized to Ni^{II} and complexed with diethyl dithiocarbamate to produce a product with a very strong UV absorption spectrum with a known extinction coefficient. The concentration of the complex is determined by UV absorption allowing the determination of the amount of Nickel Carbonyl in the original sample. By measuring the flow of the gas mixture and the time taken to collect the sample the concentration of Nickel carbonyl can be determined.

Procedure

The Nickel Carbonyl tank is connected to a bubbler containing approximately 30 ml of 1:1 nitric acid. The output from the bubbler is connected to a flowmeter to determine the flow (we used a soap bubble meter). The gas mixture was flowed through the bubbler at a rate of about 50 sccm for 30-60 minutes. The nitric acid dissolved the Nickel Carbonyl and oxidized it to Ni^{II}. The sample was washed from the bubbler into a 50 ml volumetric flask for analysis as Ni^{II}.

An aqueous solution of 0.1% sodium diethyldithiocarbamate (BDH AnalaR grade) was prepaed with water which was purified by double-distillation over $KMnO_4$ followed by passage through a Barnstead organic removal cartridge and two Barnstead mixed resin ultrapure cartridges. This solution was extracted with successive portions of carbon tetrachloride (BDH Assured, ACS grade) until the CCl_4 layer was colourless.

The pH of the 1:1 nitric acid solution was adjusted to the proper range for complexation with diethyldithiocarbamate by the addition of ammonium hydroxide (ACS grade). The pH was tested with colorpHast Indicator sticks to ensure that it was between 8.5 and 9.0. Once the proper pH was achieved, 2 mL of the sodium diethyldithiocarbamate was added and the solution was transferred to a separatory funnel. Two milliliters of carbon tetrachloride was added to the solution followed by vigorous shaking for at least two minutes. The CCl_4 layer was then collected in a 10 mL volumetric flask. The extractions were continued until the volumetric flask was filled to the mark. The electronic spectrum of this solution was then recorded over the range 300 to 500 nm using quartz cells and a Hitachi-Perkin Elmer Microprocessor model 340 spectrometer.

Discussion

The number of moles of nickel present in each sample was determined by the expression

moles of Ni = $2.84 \times 10^{-7} A_{328nm}$ (1)

based on the extinction coefficient given in Chilton's article [1]. The concentration of $Ni(CO)_4$ could then be determined by dividing this value by the product of the flow rate and time of flow.

---

[1] J.M. Chilton, Anal. Chem., 25, 1274-1275 (1953).

Conclusion

An instrument capable of measuring Nickel Carbonyl concentrations in the air down to the Ontario standards has been developed.

It has been shown to have a detection limit of 10 ppt.

A protocol for in-situ calibration from a cylinder containing Nickel Carbonyl has been developed, as has a technique for calibration of cylinders.

Acknowledgement

We are indebted to the Ontario Ministry of the Environment for support of this work and would like to acknowledge useful discussions with W.C. Tam, A. Szakolcai of the Ministry's Air Resources Branch and R. Potvin of Northeast Region.

V. Antunes and P. Sum ably performed much of the experimental work.

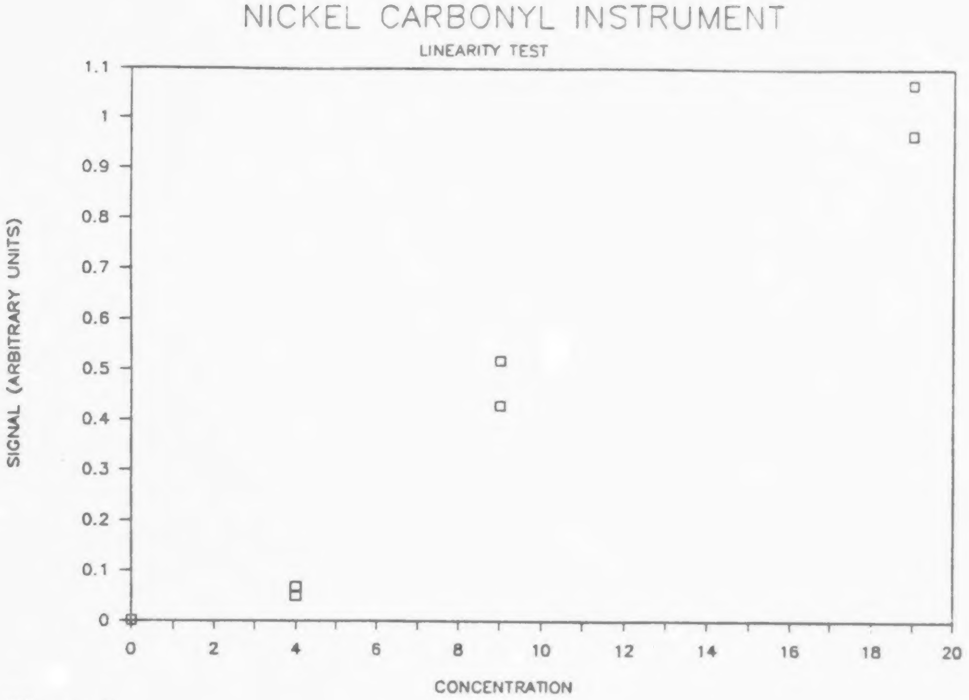


Figure I

Nickel Carbonyl instrument response showing strong non linearity

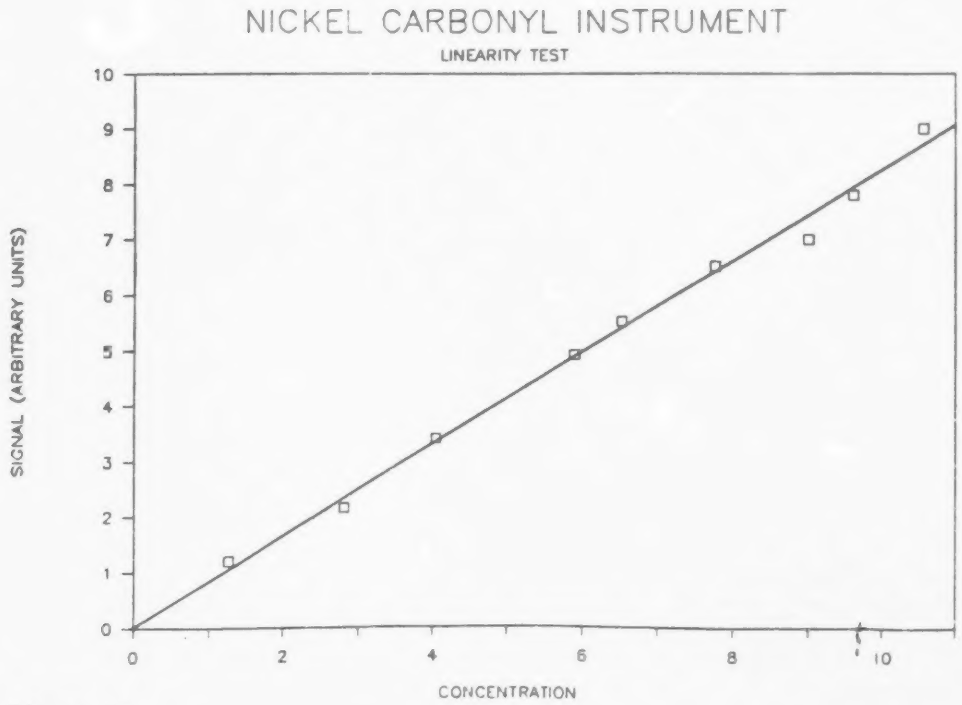


Figure II

Nickel Carbonyl instrument response using final configuration - showing linear response

"ELEMENTAL COMPOSITION OF AIR PARTICULATES INSIDE AND OUTSIDE A BUILDING".

P. Harvey, X.P. Ma, J.D. McArthur
and G. Palmer

Queen's University, Kingston
Ontario

Background

At last year's OME conference, a paper was presented which laid down much of the ground work necessary for this report.[1]) In this paper the results from the first week of a two week filtering period in June 1985 were presented. In the present paper, the results from the second week of this filtering period are analyzed. As well, some preliminary results from a recent 3 week filtering period in Feb-March 1986 are discussed.

Introduction

This project is concerned with indoor air quality and the relationship between indoor and outdoor particulate air pollution levels. Five filtering stations have been set up in and around a high school in Kingston Ontario in order to measure these effects. Three of the filters were placed in separately ventilated areas within the school, and the other two which were equipped with meteorological recording devices were placed outside, one beside the school near a busy intersection and the other in a nearby residential backyard.

The filter used was a moving 0.4µm nucleopore filter which yields a time resolution of 2 hours. These filters were analyzed using proton induced X-ray emission (PIXE) on the Queen's Van de Graaff accelerator. Elements commonly detected are Al, Si, S, Cl, Ca, Ti, Mn, Fe, Zn, Pb and Br with Na, K, Cr, Cu and Sr being detected less frequently. Our detection limits for the elemental concentrations in air are typically less than $0.03 \mu g/m^3$. The reader is referred to last years OME conference proceedings (ref 1) for a more detailed description of apparatus and analytical techniques.

General Results

Using factor analysis to organize the detected elements into groups, it was observed that the elements could generally be collected into four main classifications:

1) Dust -- This factor is responsible for about 80% of the total suspended particulate matter analyzed for the indoor filters, and consists of Si, Fe, Al, Ca, Cl, Mn, Cu, Zn and Sr. Of these, Si, Fe, Al, Ca, Mn and Sr are found in local soil samples, while the other elements (Cl, Cu and Zn) are observed mainly in indoor dust.

2) Industrial pollutants -- Sulphur is the only observed element that can be attributed to pollution by industrial sources.

3) Automotive pollutants -- Pb and Br are elements associated with automotive emissions, and are found at all sampling sites to be in approximately the ratio 5:1 which is typical of car exhaust.

4) Trace elements -- These are the elements which usually appear in concentrations close to our

detection limits. For these elements, the noise introduced by statistical fluctuations in the sampling and analysis makes categorization difficult. These elements include Na, K, Cr, Ti, Mn, Cu, Zn and Sr.

Shown in Figure 1 are example plots of the element scans for the S3 (main office) filter location in June 1985. Note the lower concentrations of the dust elements on the weekends of June 8-9 and June 15-16.

At times, in addition to these four categories, other factors can be introduced by specific human activities indoors. For example, one episode involving high indoor concentrations of Ti was attributed to spray-painting, and another with high Cu and Fe levels is thought to result from a hair spray used when one of the filters was placed in the hairdressing room of the school.

In this report, we present a model for the indoor concentrations of elements belonging to the first three categories. The formula that will be used has the following general form:

$$C_i = c_1 C_o + c_2 f(t) \qquad 1)$$

where C_i = Indoor concentration of an element.
C_o = Outdoor concentration of element.
$f(t)$ = A time varying indoor source function.
c_1, c_2 = Empirically determined constants.

Major progress has been made since last year's report by introducing a time varying function used to model the amount of each element injected into the air by human activity within the building. The following three sections of this report will be dedicated to developing the form of $f(t)$ and determining the values of c_1 and c_2 for each of the three groups of elements discussed previously.

Group 1 -- Dust

For this factor, the term $c_2 f(t)$ has been introduced due to the large amounts of dust which are stirred up by human activity within a building. An estimate of the function $f(t)$ has been made by assuming that the activity within the building is constant between the hours of 8:30 and 16:00 on weekdays, with no activity otherwise. Clearly, counting the number of people in each room at a given time would give more accurate results, but this data was not available.

Assuming that the rate at which dust is injected into the air is proportional to the activity within the building, and that the airborne dust is removed from the room or settles out of the air with a mean residence time of 2 hours, then the concentration of dust in the air on a weekday takes on the following form (t in hours):

$$\begin{aligned} f(t) &= 0\,, && 0{:}00 < t \le 8{:}30 \\ &= 1.0241*\{1-\exp[-(t-8{:}30)/2]\}\,, && 8{:}30 < t \le 16{:}00 \\ &= \exp[-(t-16{:}00)/2]\,, && 16{:}00 < t < 24{:}00 \end{aligned}$$

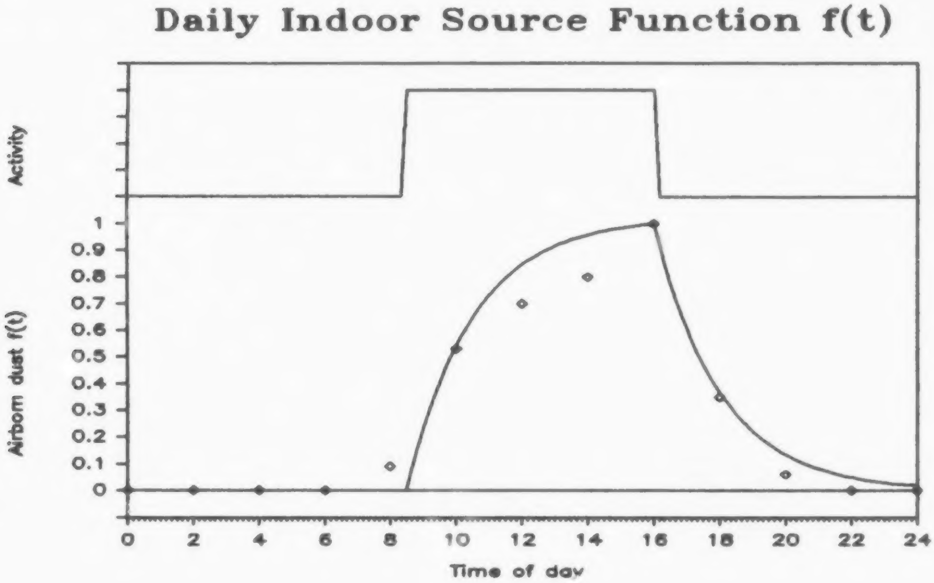


Figure 2 -- Graph of human activity and f(t) used in modelling indoor source term.

On the graph, the theoretical curve for f(t) is given by the solid line, and the experimental points correspond to an average of the indoor dust factor scores for all indoor samplers for each weekday between June 3 and June 17/85. The residence time of 2 hours was chosen so that the theoretical curve best fit the experimental data. It can be seen that f(t) is representative of the average relative amount of dust suspended indoors on weekdays. During weekends, there is assumed to be no activity.

Using multiple regression, the data from each of the indoor sampling sites was modelled by combining the activity function and the elemental concentration as measured in the schoolyard using formula 1). For the soil elements, the coefficient c_1 is expected to be the lowest since natural particles typically have larger diameters than particles from anthropogenic sources, and the filtering efficiency of the ventilation system is higher for the larger particles. Table 1 gives the derived values for c_1 and c_2 for Al (considered here to be representative of the natural dust elements). The errors given represent only those in the multiple regression fit, and not errors in the data itself. Also given is a correlation coefficient between the resulting scan and the experimental elemental scan. (See figure 3 for a plot of the fit obtained for S3.)

Table 1

	c_1	c_2 ($\mu g/m^3$)	corr
S1 - Business room	0.15 ± 0.02	0.09 ± 0.02	0.468
S2 - Modelling room	0.12 ± 0.02	0.09 ± 0.02	0.301
S3 - Main office	0.15 ± 0.02	0.25 ± 0.02	0.727

The activity coefficient c_2 is largest for the office. One reason for this is that the office is carpeted, and the carpet serves as a dust reservoir from which the soil elements are repeatedly suspended. For the other rooms, the activity was not as uniform from day to day, so the fits to these data were not as good as for the office (this is illustrated by the correlation coefficients shown). The indoor/outdoor ratio c_1 was similar for all rooms. Any variations can be attributed to the different ventilation systems of the three rooms. In June, this coefficient should be higher than during the other filtering period of late February because of open windows and doors during the warm weather of June.

Group 2 -- Industrial pollutants

Modelling the indoor levels for sulphur is simpler than for the soil elements since during the summer, the indoor source term is found to be zero for this element. Therefore, the indoor sulphur concentration can be modelled as simply a constant fraction of the outdoor sulphur level. The coefficients c_1 and correlation coefficients between the indoor and outdoor scans are given below in table 2, and figure 4 shows the type of fit obtained for S1.

Table 2

	c_1	corr
S1 - Business room	0.86 ± 0.03	0.830
S2 - Modelling room	1.06 ± 0.02	0.919
S3 - Main office	0.55 ± 0.02	0.761

For all cases, the correlation coefficients are high indicating a strong similarity between the trends in the outdoor sulphur levels and those indoors. The above indoor/outdoor ratio, c_1, is found to be much higher than the average of 0.14 for the soil elements. This is a result of the smaller average particle diameter and therefore the poorer ventilation filtration expected for sulphur.

In an attempt to better isolate the source of sulphur emissions, a number of air parcel back trajectories were obtained from Atmospheric Environment Services, Toronto for the times around the high sulphur episode on June 8-9. These trajectories are shown in figure 5. From this survey, it became apparent that the most likely source of the sulphur detected during this period is the industrial area to the south of lake Erie. A scanning electron microscope study confirmed the particulate size distribution on these filters to be in the range of 0.2-0.6μm in diameter. This corresponds to the small particle size expected for a combustion source, and which is necessary for long range transport.

Group 3 -- Automotive emissions

For this group of elements, again it is found that there is no appreciable periodic indoor source term, so the indoor concentrations of Pb and Br will be modelled according to the outdoor concentrations. For Pb and Br, it is found that the indoor concentrations correlate more strongly with the backyard outdoor levels. This is due to the close proximity of the schoolyard sampler to a source of automotive exhaust. Since this sampler is within 100m of a major traffic intersection, the Pb/Br levels recorded there exhibit unusually large fluctuations. Therefore, the data from the backyard filter was used to model the detected indoor Pb/Br particulate concentrations.

Table 3 shows the values of c_1 for Pb, as well as correlation coefficients between the indoor and the backyard Pb levels, and figure 6 shows the fit obtained for the S2 filter location. Note the indoor peak in Pb level occurring on June 5 in figure 6 with no corresponding peak in the outdoor Pb level. For this peak, the indoor Pb level reaches a maximum value of about 1.4 $\mu g/m^3$ off the top of the graph. Since a coincident Br peak was observed inside in a ratio indicative of automotive exhaust, this peak is attributed to an indoor source of automobile emissions. This is likely a result of the doors to the auto shop (which is in the next room) being left open. In performing the linear regression and correlation, this high indoor peak was removed from the data set in order to avoid biasing the indoor/outdoor ratio c_1.

Table 3

	c_1	corr
S1 - Business room	0.56 ± 0.03	0.796
S2 - Modelling room	0.63 ± 0.02	0.808
S3 - Main office	0.41 ± 0.02	0.728

In agreement with the c_1 coefficient for sulphur, the modelling room has the lowest filtering efficiency (yielding the highest indoor/outdoor coefficient, c_1) of all indoor filtering locations. This chart also shows that the filtering efficiency of the ventilation system is higher for Pb than for sulphur, which implies that the sulphur generally resides on smaller particles than the Pb. This hypothesis has been confirmed by scanning electron micrograph studies.

Recent developments

The filters collected in this year's Feb-Mar sampling period have so far only been analyzed to the point of obtaining the element scans. As yet, no modelling has been done on this data, so this section of the report will discuss only trends in the data. Indoor/outdoor ratios and activity coefficients have not yet been calculated.

Shown in figure 7 are the element scans for the S3 filter location for the period Feb 20 - March 6/86. Some interesting differences in this data can be observed. Firstly, the dust elements seem to be split into two distinctive groups, with the Si, Fe, Zn, Ti group appearing in high concentrations every weekday, but the Ca, Cl, Cu, S group only appears on certain weekdays. (The elements Ca and Cl do appear in the first group in roughly the same proportions as during the June sampling period, but they appear in the second group in concentrations that are higher by factors of about 3 and 5 respectively.) It is apparent that there is a link between these two groups for at least some days during the week. Why this link was broken on Feb. 21, 25 and March 5 can now only be speculated. Possibly this could be a result of the doors to the office being closed on those days (the office doors are normally left open). Closing the office doors would yield the observed results if the office dust was deficient in Ca, Cl, Cu and S while the dust in the neighbouring hallway was rich in these elements. The high Ca and Cl levels in the hallway could be explained by the large number of people tracking road salt (containing $CaCl_2$) into the hallway from outside, whereas relatively few people would enter the office after just being outside.

It is interesting that during this sampling period the sulphur is found to have a strong indoor source term, while during the June filtering session there was no measurable indoor sulphur coefficient. The difference may be related to the source of Ca and Cl in the hallway. The amount of sulphur in snow due to acid precipitation has been measured to be about 1000 ng/g for sites on Montreal Island.[2]) If the snow in the Kingston area has a comparable sulphur content, then it is possible that the sulphur from snow is deposited on dust particles as the snow melts and evaporates in the hallways of the school. It should be noted, however, that the outdoor sulphur levels still have an appreciable effect on the indoor air. The effect of the outdoor sulphur levels for this period can be seen on March 3-4 when the outdoor sulphur level gradually built up to a peak at about midnight on March 4. Also, the effect of a peak in the outdoor sulphur level occurring in the afternoon of Feb. 23 can be observed in the sulphur scan of figure 7.

Looking at the outdoor element scans for the Feb-March sampling period, the amount of airborne dust is lower on average by a factor of 2-3 than for the corresponding location during the June run. This was expected, and is due to the snow cover which suppresses the injection of dust into the air by a strong wind as was observed in June/85.

Summary

Using a simple two term model, the indoor particulate concentrations for most elements detected have been adequately explained. For the anthropogenic pollutants, Pb, Br and S, only one term was necessary for the data taken during the June filtering period, and the indoor concentrations for these elements could be described as a constant fraction of the corresponding outdoor concentration. For the naturally occurring elements, a second term was necessary in order to model the daily variations in the concentrations of the elements found in the indoor dust due to human activity within the building. The form of the function used in this term was approximated theoretically, however no allowance for day to day fluctuations in the indoor activities was made. The result was a good prediction of the general trends of the elemental composition of indoor suspended particulate matter for both anthropogenic and naturally occurring elements.

References

1) J.D. MacArthur, P.J. Harvey, G.R. Palmer and X-P Ma, **The Exchange of Air Particulates Between the Inside and Outside of a Building**, Proc. Technology Transfer Conference #6, Ontario Ministry of the Environment, 1985, Part 1, pp. 320-334.

2) R.E. Jervis and S. Landsberger, **Trace Elements in Wet Atmospheric Deposition**, Intern. J. Environ. Anal. Chem., 1983, Vol 15, pp. 89-106.

3) R.A. Wadden and P.A. Scheff, Indoor Air Pollution, Wiley, 1983.

4) The Case Against the Rain, Ontario Ministry of the Environment report, 1980.

5) V. Valkovic, Trace Element Analysis, London, 1975.

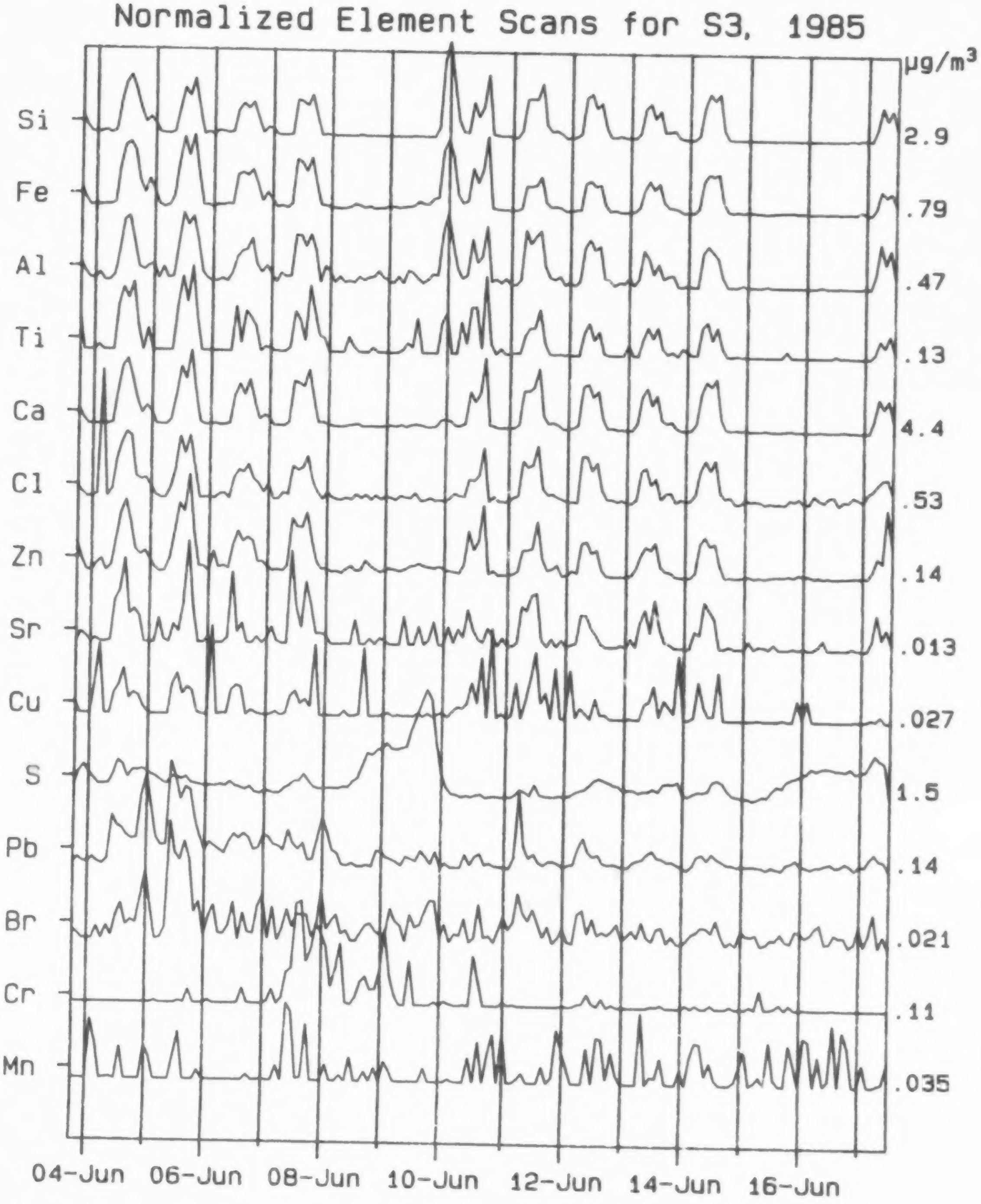


Figure 1 - Indoor element scans for the S3 (main office) filter location for the June/85 sampling period. All scans have been normalized to the same standard deviation, and have been separated by 4 standard deviation units. This separation is given on the right in µg/m³ for each scan.

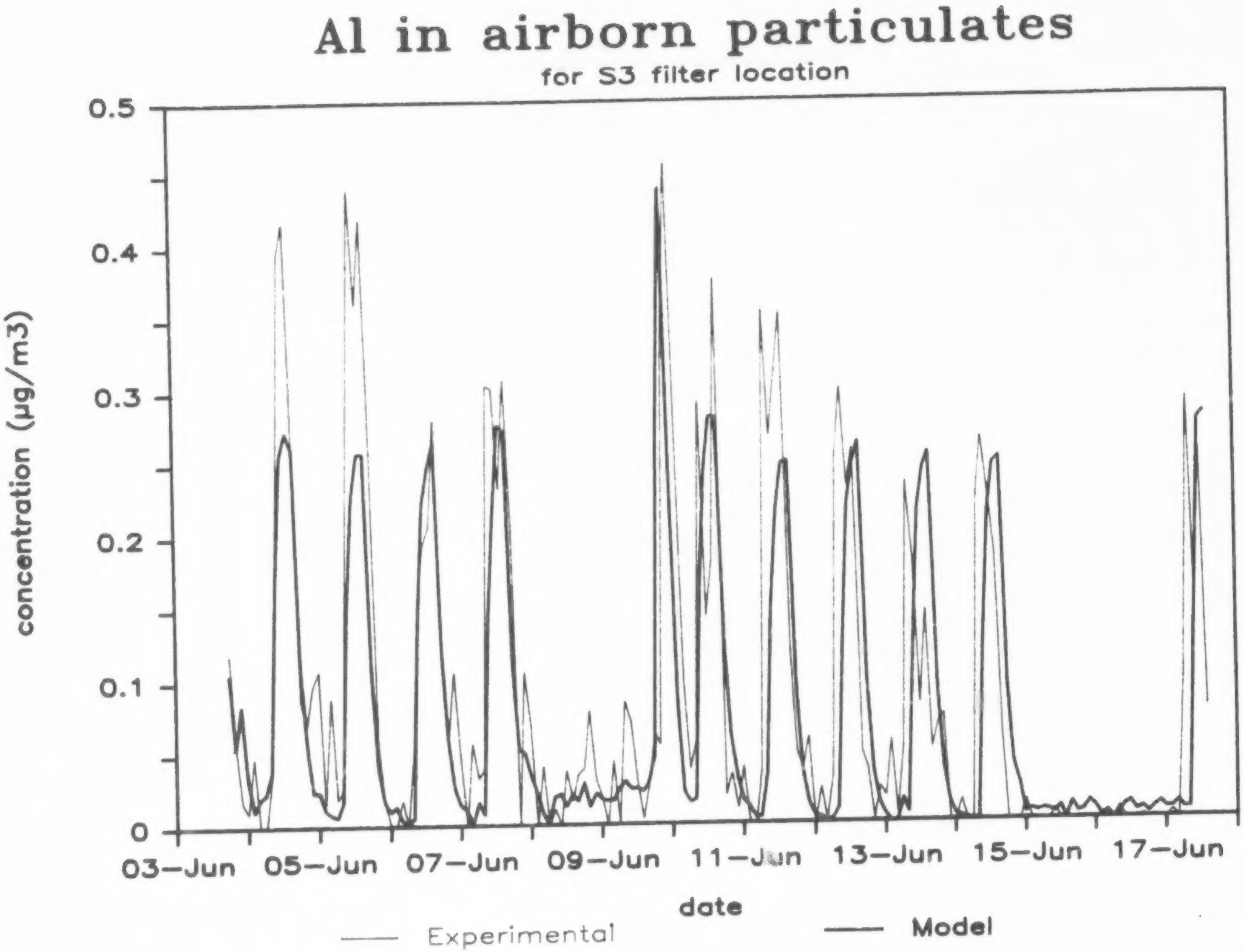

Al in airborn particulates
for S3 filter location
0.5
0.4
0.3
0.2
0.1
0
concentration (µg/m3)
03–Jun
05–Jun
07–Jun
09–Jun
11–Jun
13–Jun
15–Jun
17–Jun
date
Experimental
Model

Figure 3

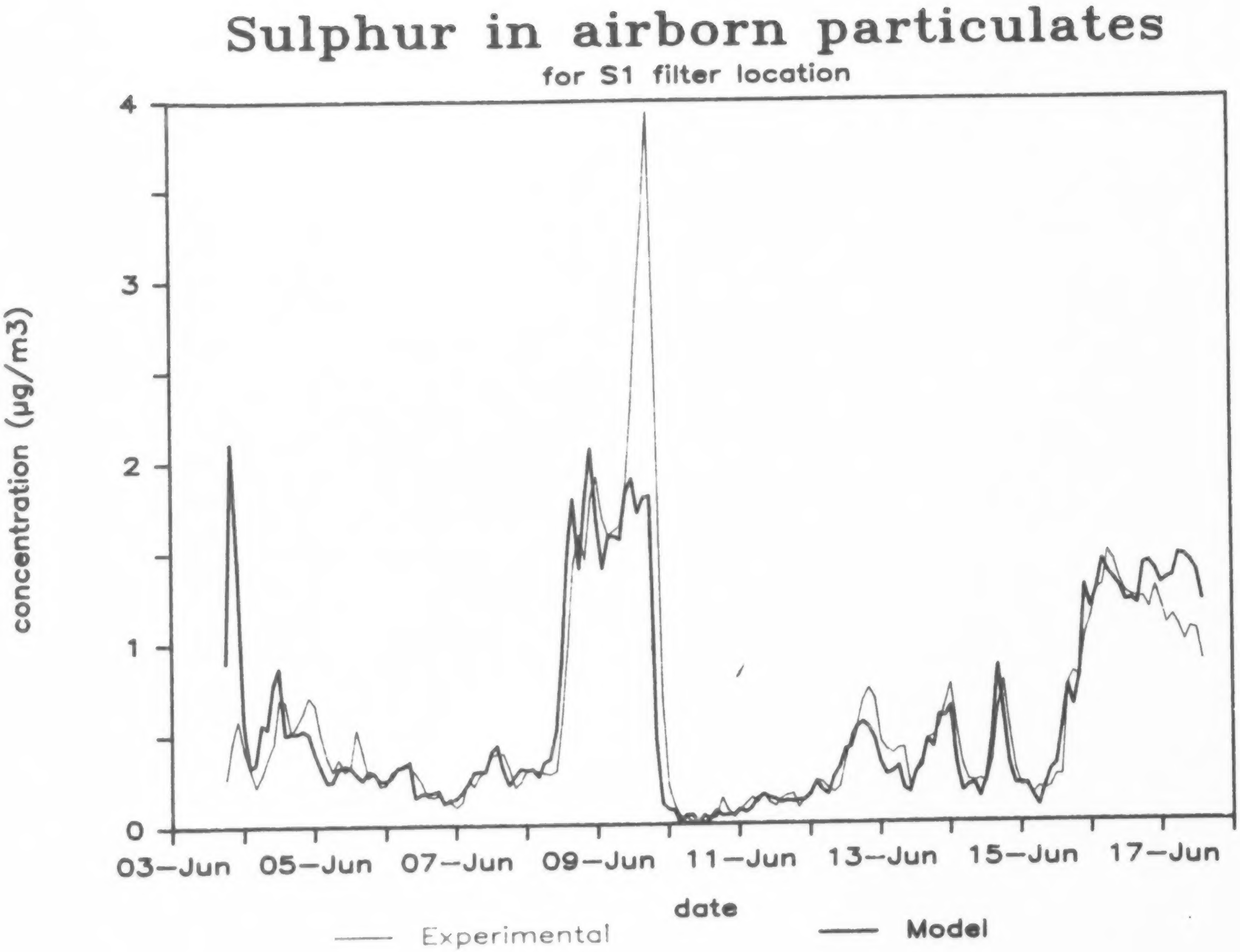
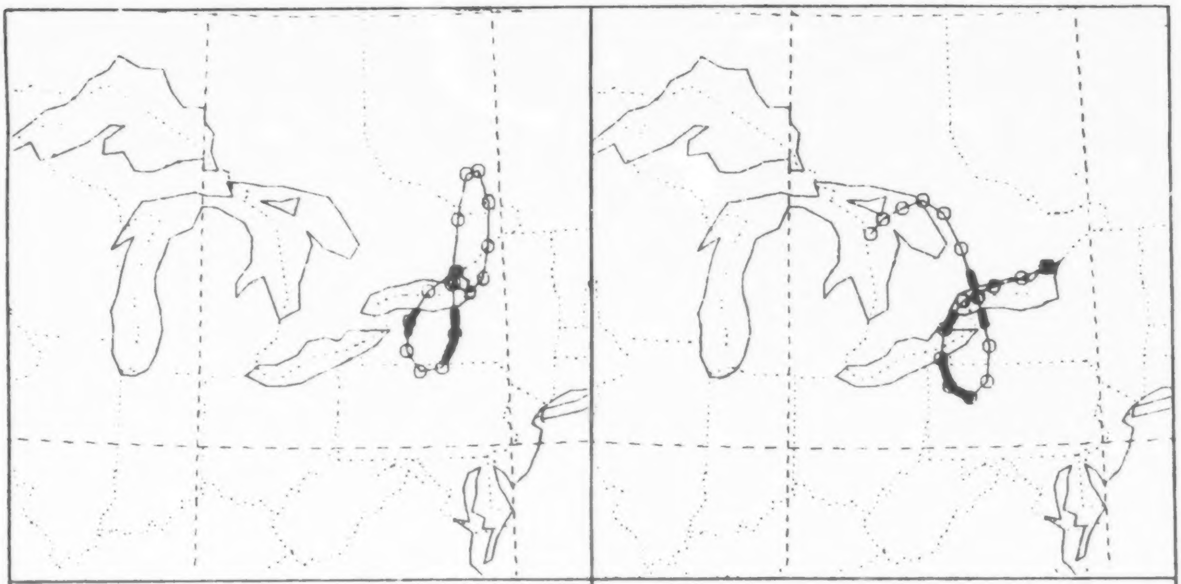
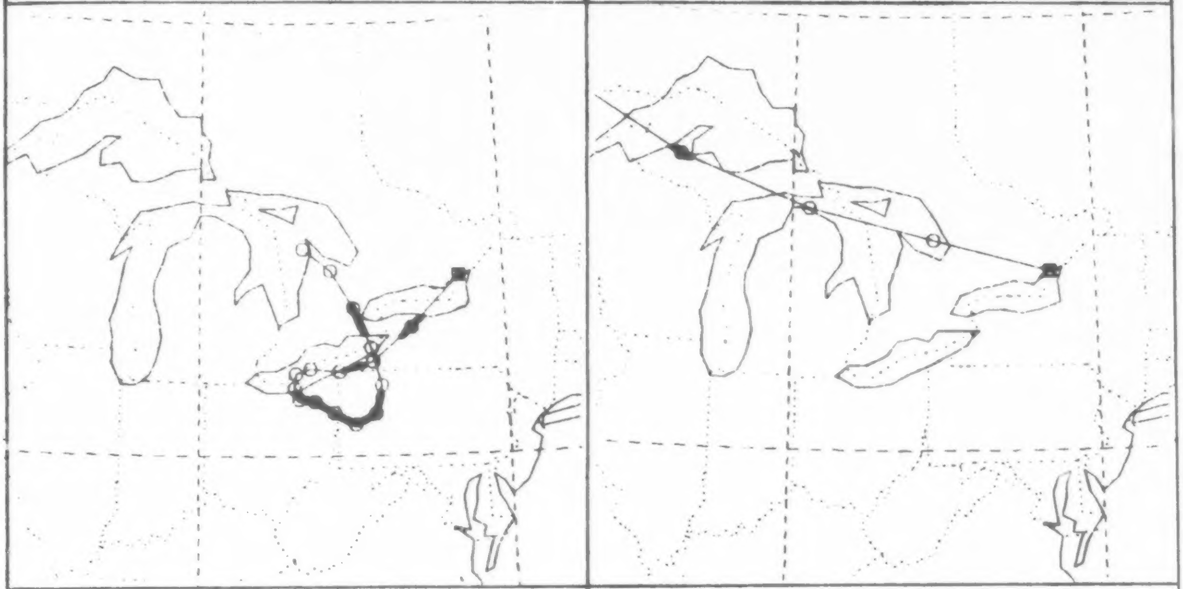

Sulphur in airborn particulates
for S1 filter location
concentration (µg/m3)
0
1
2
3
4
03–Jun
05–Jun
07–Jun
09–Jun
11–Jun
13–Jun
15–Jun
17–Jun
date
Experimental
Model

Figure 4



8: 00am Sat June 8/85
0.39 $\mu g/m^3$

8: 00pm Sat June 8/85
2.37 $\mu g/m^3$



2: 00pm Sun June 9/85
4.29 $\mu g/m^3$

2: 00am Mon June 10/85
0.0 $\mu g/m^3$

Figure 5 - Four day air parcel back trajectories for the 925mb pressure level. Darkened areas along trajectory paths indicate when the airmass passed over areas of industrial activity. Sulphur levels recorded in Kingston are given in $\mu g/m^3$ for each trajectory.

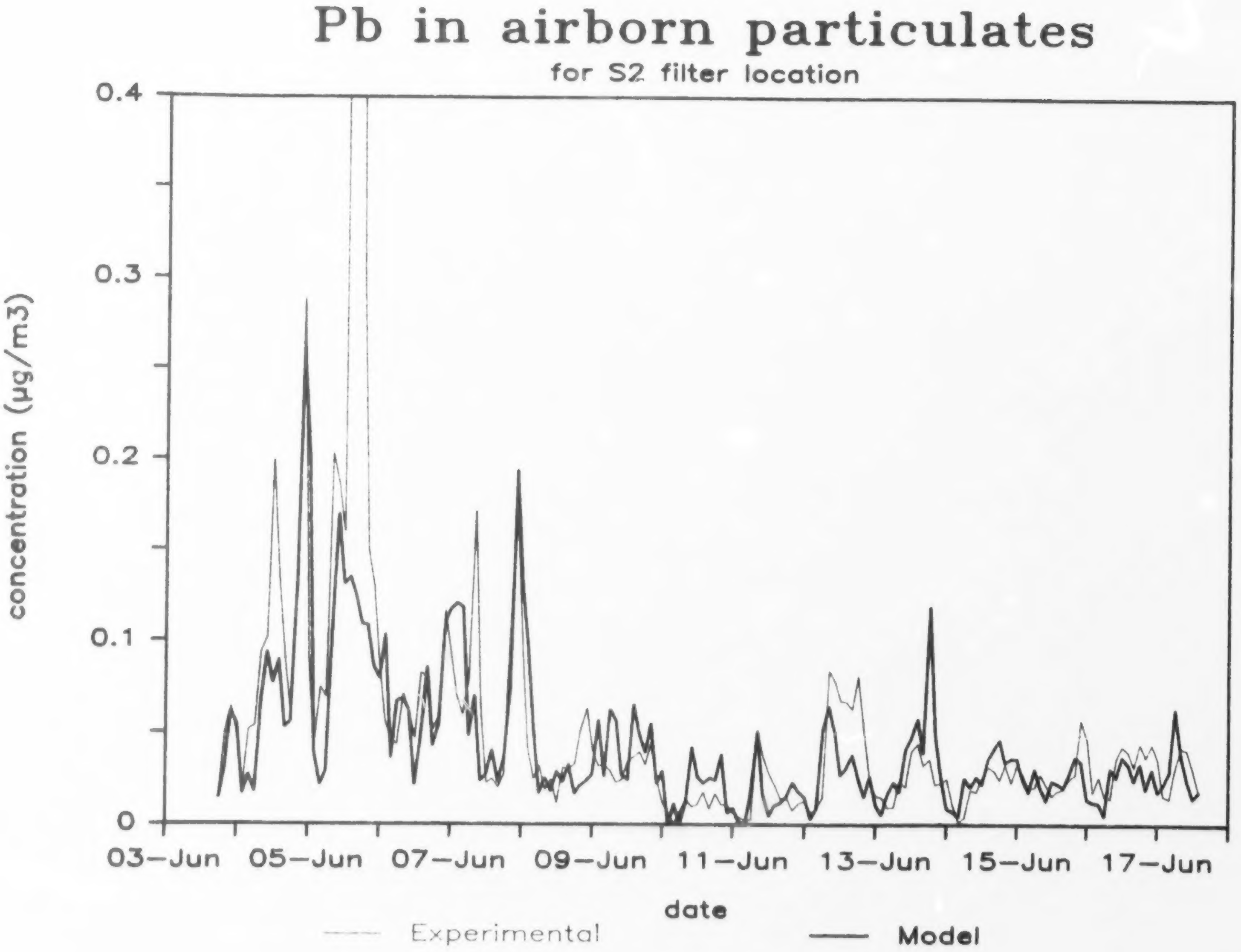

Pb in airborn particulates
for S2 filter location
concentration (μg/m3)
0.4
0.3
0.2
0.1
0
03–Jun
05–Jun
07–Jun
09–Jun
11–Jun
13–Jun
15–Jun
17–Jun
date
Experimental
Model

Figure 6

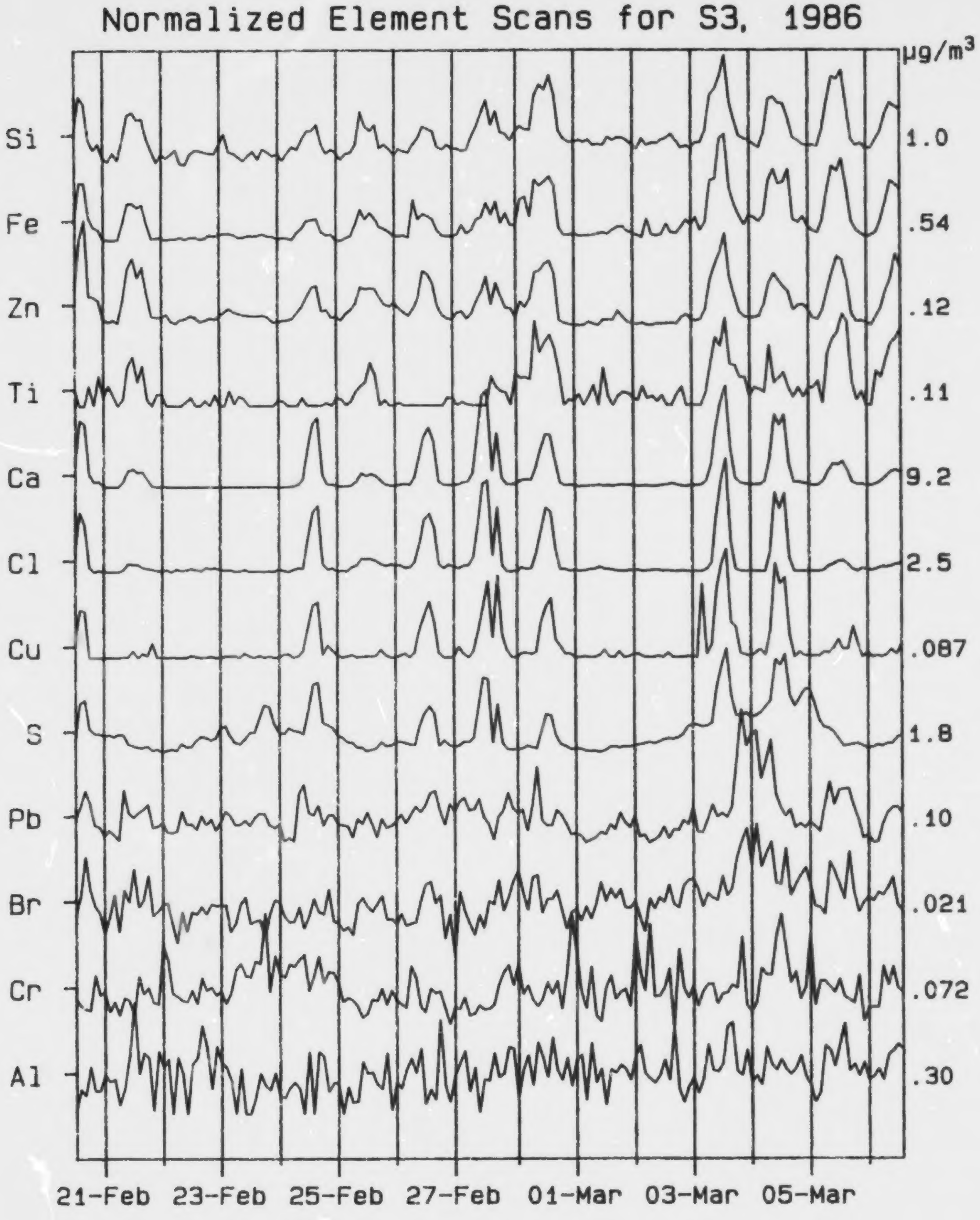


Figure 7 - Indoor element scans for the S3 (main office) filter location for the period Feb. 20 to March 6, 1986. All scales have been normalized to the same standard deviation, with the numbers to the right giving the separation between scans in terms of the individual element concentrations in µg/m³

STUDY OF THE THERMAL REACTIONS OF POLYCHLORINATED DIBENZO-P-DIOXINS ON FLYASH PARTICLES UNDER INCINERATOR CONDITIONS

by

L.C. Dickson and F.W. Karasek
The Guelph-Waterloo Centre for Graduate
Work in Chemistry, Waterloo, Campus
University of Waterloo
Waterloo, Ontario
N2L 3G1

SUMMARY

All incinerators burning municipal waste produce chlorinated dioxins. The mechanism by which these compounds are formed is unknown. Experiments were performed that show these compounds can be produced from known precursors by surface catalysed reactions on the flyash particulates present in the incineration process. A full range of the tetra- through octachlorinated dibenzo-p-dioxins were produced from ^{13}C-labelled pentachlorophenol and two trichlorophenols on the surface of flyash from an Ontario municipal incinerator that had been previously freed from organic material. A simple flow tube apparatus at 300°C under a 10mL/min. nitrogen flow was used for the experiments. The use of ^{13}C-labelled pentachlorophenol gave a direct measure of the extent of the catalytic reactivity of the flyash surface. Much lower amounts of chlorinated dioxins were produced in similar experiments with flyash from a modern Japanese incinerator whose effluents are normally extremely low in these compounds. Only small amounts of octachlorodioxin, the thermal condensation product expected, were formed using ground firebrick or an empty flowtube for the reactive surface. These results indicate that the flyash surface has constituents and properties that promote the production of chlorinated dioxins from chlorinated phenols and support the catalyzed surface reaction mechanism previously proposed.

INTRODUCTION

The incineration of municipal refuse has become an attractive alternative to the practice of dumping refuse in landfill sites. Incinerating refuse in plants close to urban areas offers the advantages of low transportation costs, reduction in the volume of solid wastes and the possibility of energy recovery. However, the incineration of refuse and combustion processes in general emit potentially hazardous substances into the environment. In a review of organic compounds found in incinerator effluent, Junk and Ford listed over 330 substances, including aliphatics, polynuclear aromatic hydrocarbons, substituted benzenes, carbonyl compounds and sulphur and nitrogen-containing compounds (1).

Since 1977 when Olie discovered chlorinated dibenzo-p-dioxins and chlorinated dibenzofurans in the effluent of a municipal incinerator in the Netherlands, attention has been focused on these toxic compounds (2). Chlorinated dioxins have since been found in flyash from incinerators located in Canada, Japan, Switzerland, France, Norway and the United States (3-7). These compounds are of considerable public concern because certain isomers (e.g. 2,3,7,8-tetrachlorodibenzo-p-dioxin) are extremely toxic and can cause liver damage and chloracne (8).

Discussions of thermal formation of dioxins have generally dealt with gas-phase reactions and extrapolation from the liquid phase to the gas phase. Three general mechanisms have been proposed:

1. survival of trace levels in the fuel,

2. generation from precursors such as chlorinated phenols,

3. de novo synthesis from chemically dissimilar compounds and sources of chlorine (9).

However, reports by Shaub and Tsang have made strong arguments in favour of heterogeneous gas-solid phase reactions as the source of chlorinated dioxins from incineration (10-12). Computer simulations based on models of homogeneous gas phase mechanisms predict lower levels of chlorinated dioxins and chlorophenates than are found in incinerators (11). Therefore heterogeneous gas-solid reactions which have much more favourable kinetics than radical reactions at lower temperatures must be considered. Flyash has many Lewis and Bronsted acid and base sites. A chemisorbed precursor molecule could become very reactive, due to the removal of H or Cl from the bound molecule by fast abstraction by gas-phase radicals or by neighbouring reactive sites on the flyash (12). The activation of the phenol by adsorption, possibly through the hydroxyl group, could be similar to that seen by Sanderman and coworkers, who reported that the pyrolysis of the sodium salt of pentachlorophenol gave much larger yields of octachlorodioxin than the pyrolysis of pentachlorophenol alone (13). Experiments using chlorinated dioxins adsorbed onto flyash have shown that gas-solid phase chlorination of dioxins is rapid and efficient (14-17).

In this study chlorinated phenols were passed through a bed of municipal incinerator flyash at 300°C. Tetrachloro- through octachlorodioxin reaction products were detected in the flyash extract and downstream impinger.

EXPERIMENTAL

Chemicals and Standards: Pentachlorophenol was purchased from Aldrich Chemical (Milwaukee, Wis.). 2,4,5-trichlorophenol and 3,4,5-trichlorophenol were purchased from Fluka (Caledon Labs, Georgetown, Ont.). Unlabelled chlorinated dibenzo-p-dioxin standards were supplied by the Ontario Ministry of the Environment. $^{13}C_{12}$-labelled tetrachlorodioxin and octachlorodioxin were purchased from Cambridge Isotopes Labs (Woburn, Mass.) and labelled pentachlorophenol from MSD Isotopes (Dorval, P.Q.). All chemicals were 98% pure or better. All solvents were of "Distilled in Glass" grade (Caledon Labs, Georgetown, Ont.). Chromosorb P Non-Acid Washed chromatographic support derived from crushed firebrick was purchased from Johns-Mansville (Denver, Colo.).

Flyash: Flyash from a refractory-wall mass-burning municipal refuse incinerator in Ontario was supplied by the Ontario Ministry of the Environment. Machida flyash from a modern fluidized-bed municipal refuse incinerator in Japan was supplied by Dr. H. Hatano, Kyoto University, Kyoto, Japan.

Apparatus and Glassware: The apparatus is shown in Figure 1. All glassware was made of Pyrex.

Glassware was washed in an ultrasonic bath for approximately thirty minutes using a mild detergent. Following rinsing with deionized water, glassware was dried overnight in an oven at 240°C. Before use glassware was rinsed with solvent. Soxhlet extraction apparatus was rinsed by refluxing benzene for two hours. The rinse benzene was discarded and fresh benzene used for the flyash extraction. This procedure has been shown effective in removing background impurities from laboratory glassware.

Experimental Procedure: About 20g of exhaustively extracted flyash was placed in the reservoir. This flyash had been heated overnight in the flowtube at 340°C under a 150 mL/min. flow of nitrogen to remove any residual organic material. A bed of glass beads about 35mm in depth was placed in a section of pyrex tube which had a coarse glass frit in one end. The glass beads were retained with a plug of glass wool. 100uL of a 1 mg/mL chlorinated phenol solution in methanol was deposited onto the glass beads and the solvent allowed to evapourate. The tube was fitted to the reservoir with the frit and glass beads just upstream of the flyash. Attached to the other end of the reservoir was a long-armed impinger of 200 mL capacity. This impinger is similar in design to the one used in the Ames Vapour Sampling System (18). The apparatus was placed in a modified gas chromatographic oven. The impinger resided outside the oven and was cooled with a saturated salt-water-ice bath. A guard trap containing florisil was attached to the outlet of the impinger. The oven was heated to 300°C over twenty minutes then a 10 mL/min. flow of high-purity nitrogen was passed through the flow tube for one hour, maintaining the 300°C temperature throughout. After the experiment was complete the nitrogen flow was stopped and the oven quickly cooled to room temperature. The impinger was removed and the ends sealed with aluminum foil. After rinsing the outside surface of the reservoir with solvent, it was placed in a soxhlet extractor and the organic compounds extracted with 300 mL benzene for 18 hr. The inside surfaces of the impinger were rinsed with 75 mL of dichloromethane, which was transfered to a 300 mL round bottom flask. The extracts were reduced to several mL by rotary evapouration under reduced pressure. In the event that particulate matter was suspended in the extract after rotary evapouration, the extract was transfered to a centrifuge tube and centrifuged to drive the particles to the bottom. The extract was transfered to a pear-shaped flask and concentrated further. Final concentration to 100 uL was achieved by flowing a gentle stream of high purity nitrogen over the surface of the sample in a calibrated 1 mL reactivial.

Gas Chromatographic Analysis: To screen the flyash extracts and impinger rinses for chlorinated reaction products samples were analysed on a Hewlett-Packard HP-5880 gas chromatograph equipped with an electron capture detector and a cool on-column injector. A 30m X 0.32mm I.D. DB-5 fused silica capillary column (J & W Scientific, Rancho Cordova, CA, U.S.A.) was used.

Gas Chromatographic / Mass Spectrometric Analysis: Analyses were carried out on a Hewlett-Packard 5987A gas chromatograph/mass spectrometer (GC/MS) with an HP1000 data system. The instrument was equiped with a cool on-column injector, a fused silica 30m X 0.32mm I.D. DB-5 column and a direct inlet GC/MS interface. Instrument operating parameters are given in Table I. Quantitation of chlorinated dioxins was carried out in electron impact selected ion monitoring (EISIM) mode. Three isotope ions (M, M+2, M+4 or M+2, M+4, M+6 were monitored for tetra to octachloro-p-dioxins.

The standard mixture used for external standard quantitation of dioxins contained one isomer each of tetra, penta, hexa, hepta and octachlorodibenzo-p-dioxins. Identification of compounds was confirmed using the following criteria:

1. The mass chromatographic peaks must fall within a retention time window established for a specific class of isomers.
2. The mass chromatographic peaks produced by the component must exhibit the correct ratios of intensities of ions being monitored.
3. The signal-to-noise ratio must be greater than 3.

The retention time windows were determined by using mixtures of available isomeric compounds.

RESULTS AND DISCUSSION

Labelled ^{13}C-pentachlorophenol was passed through a flowtube containing either Ontario flyash or Machida flyash at 300°C using a flow of 10mL/min N2 maintained for one hour. The GC-ECD analyses of the flyash extracts are shown in figure 2. The top chromatogram is an analysis of the extract of the Ontario flyash, the second an analysis of the extract of the Machida flyash. The bottom plot is an analysis of a standard solution containing tetrachloro- to octachlorodioxins and furans at an average concentration of 2 nanograms per microlitre. The peaks in the chromatograms represent reaction products or the unreacted labelled phenol. Compounds eluting below 200 degrees Celcius are mostly chlorinated benzenes and chlorinated phenols. The compounds eluting above this temperature are the result of the condensation of the chlorinated phenol and other molecular reactions which followed. The experiment using the Ontario flyash yielded much larger amounts of some reaction products than that using Machida flyash. These reaction products elute in the retention time windows characteristic of chorinated dioxins and furans.

The chromatograms from the EISIM analyses of the flyash extract and the impinger rinsings from the experiment using Ontario flyash is shown in figure 3. The plots were produced by merging the selected ion abundance profiles (SIAP) of the most abundant ion from the molecular ion isotope cluster of each $^{13}C_{12}$-labelled chlorinated dibenzo-p-dioxin. The use of a labelled precursor eliminates interferences from possible unextracted compounds on the flyash. It is clear that chlorinated dioxins were formed in-situ on the surface of the flyash from the pentachlorophenol precursor. Octachlorodibenzo-p-dioxin is likely formed first by the condensation of two phenol molecules. The other chlorinated dioxins arise through the dechlorination of the higher chlorinated species.

The chlorinated dioxins appearing in the impinger rinsings are mainly the tetra- and pentachlorinated isomers. These more volatile compounds are desorbed from the flyash and are carried downstream by the nitrogen flow to condense in the cooled impingers. It has been recently demonstrated that chlorinated dioxins will desorb from flyash surfaces under similar conditions of temperature and flow (19).

The results of the EISIM analyses of the flyash extracts and impinger rinsings from the experiment using Machida flyash is shown in figure 4. The chlorinated dioxin elution pattern in the flyash extract is remarkably similar to that of the Ontario flyash. The peak at 26.5 minutes in the analyses of the flyash and the impinger rinsings is an impurity, likely a phthalate ester.

The amounts of chlorinated dioxins formed from labelled pentachlorophenol are shown in figure 5. The experiment using Ontario flyash produced almost ten times as much chlorinated dioxins as the Machida flyash. It would appear that the latter flyash has a lower catalytic activity than the Ontario flyash. This could be due to differences in the composition of the incinerator fuel feeds or differences in the design and operating conditions of the incinerators.

Both Ontario and Machida flyashes provide a large surface area on which reactions could take place. To determine whether a large surface area is sufficient to produce the large number of isomers observed from reactions of pentachlorophenol, the precursor was passed through a bed of ground firebrick and through an empty flowtube. The results of these experiments are shown in figure 6. The chromatograms are from EISIM analyses of the impinger rinsings from experiments using Ontario flyash, firebrick and an empty flowtube. The Ontario flyash trace shows a large amount of chlorinated dioxins being formed as compared to the empty flowtube or the firebrick experiments. In the latter two experiments, the majority of the chlorinated dioxins were in the form of octachlorodibenzo-p-dioxin, the least toxic isomer of the chlorinated dioxins. The experiment with the Ontario flyash produced tetra- through octachlorodibenzo-p-dioxins.

It is clear that surface area is not a factor in producing large numbers of dioxin isomers from pentachlorophenol. The ground firebrick has a specific surface of 3.8 m^2/g, which is comparable to the Ontario flyash specific surface area of 3.2 m^2/g and the Machida flyash specific surface area of 2.2 m^2/g . These surface areas are orders of magnitude smaller than those of heterogeneous catalysts. These results indicate that the flyash surface has constituents and properties that promote the production of chlorinated dioxins from pentachlorophenol.

The total amounts of chlorinated dioxins formed using flyash, firebrick and the empty flowtube are presented in figure 7 for comparison. Octachlorodibenzo-p-dioxin and heptachlorodibenzo-p-dioxins constitute over seventy-five percent of the 3200 nanograms of chlorinated dioxins produced on the flyash. Approximately 40 ng, 100 ng and 400 ng of tetra-, penta- and hexachlorodibenzo-p-dioxins were produced, respectively. Only using an empty flowtube was there a significant amount of octachlorodibenzo-p-dioxin produced, whereas the firebrick alone produced almost immeasureable amounts. Since the amounts of octachlorodibenzo-p-dioxin produced using firebrick and an empty flowtube correspond to that produced purely by thermal condensation, clearly the catalytic constituents of the flyash promote the condensation of the chlorinated phenols to octachlorodibenzo-p-dioxin. The total amount of chlorinated dioxins produced on flyash was ten times the amount produced by the experiment using an empty flowtube. It was expected that the firebrick and empty flowtube experiments would have produced similar amounts of octachlorodioxin. The difference, we speculate, may be due to the firebrick inhibiting the condensation of the chlorinated phenol.

Having established that Ontario flyash will catalyse the production of chlorinated dioxins from pentachlorophenol, the experiments were repeated using 2,4,5-trichlorophenol and 3,4,5-trichlorophenol. The results of these experiments are shown in figure 8. These chromatograms are made from EISIM analyses of the impinger rinses. The distributions of the dioxin isomer from these chromatograms are clearly very different. The experiments using 2,4,5-trichlorophenol produced mainly hexachlorodibenzo-p-dioxins and very little of the tetra- and octa-chlorinated isomers. Also, within each congener group there are several peaks whose relative abundances are greater than those found in the experiments using pentachlorophenol or in the analyses of chlorinated dioxins extracted from the Ontario flyash before treatment. This would indicate that there are certain isomers whose production is favoured over the others, implying that certain positions on the benzene rings are more reactive to chlorination or dechlorination than the others.

The experiment using 3,4,5-trichlorophenol yielded very interesting results, in that dioxins were formed at all from a chlorinated phenol that did not possess a chlorine atom ortho to the hydroxyl group. Condensation and ring closure to form dioxins from chlorinated phenols requires ortho-substitution. Some scrambling of the chlorine and hydroxyl group positions must take place for dioxins to be formed from this precursor. The dioxin isomer distribution is very different from the distributions arising from 2,4,5-trichloro- and pentachlorophenol. The major peaks are octachlorodibenzo-p-dioxin and 1,2,3,4,5,6,7,8-heptachlorodibenzo-p-dioxin. The relatively small amount of the other heptachloro isomer suggests that the 9-position on the dioxin molecule is less easily chlorinated that the 8-position. The lesser chlorinated isomers were present only at very low levels, with pentachlorodibenzo-p-dioxin detected at the detection limit of 100 pg/uL (100 uL total sample volume).

The total amounts of each dioxin congener group produced in the experiments using penta-, 2,4,5-tri- and 3,4,5-trichlorophenol are shown in figure 9. The major reaction products from the 2,4,5-trichlorophenol isomer are hexa- and heptachlorodibenzo-p-dioxins. Considering that chlorination and dechlorination are competing processes, it would be expected that these dioxins possessing a degree of chlorination midway between the tetrachlorodibenzo-p-dioxins - the condensation product - and octachlorodibenzo-p-dioxin would predominate. The large amount of the octachlorinated and heptachlorinated isomers produced using 3,4,5-trichlorophenol and the lack of any significant amounts of pentachlorodibenzo-p-dioxin would indicate a different route to the dioxins than that taken by the other chlorinated phenols possessing an ortho-substituted chlorine. The phenol may undergo rearrangement or isomerization due to dechlorination, dehydrogentation, transchlorination and other similar molecular reactions before condensation to form a chlorinated dioxin. The various competing reactions and the reactivity of the intermediates would be reflected in the amounts and kinds of isomers formed.

REFERENCES

1. G.A. Junk and C.S. Ford, Chemosph., 9 (1980) 187
2. K. Olie, P.L. Vermeulen and O. Hutzinger, Chemosph., 8 (1977) 455
3. G.A. Eiceman, R.E. Clement and F.W. Karasek, Anal. Chem., 51 (1978) 2343
4. H.R. Buser, H.P. Bosshardt and C. Rappe, Chemosph., 7 (1978) 165
5. L.L. Lamparski and T.J. Nestrick, Anal. Chem., 52 (1980) 2045
6. A.C. Viau, S.M. Studak and F.W. Karasek, Can. J. Chem., 62 (1984) 2140
7. F.W. Karasek, K.P. Naikwadi and H.Y. Tong, (in press), Proc. of Machida Workshop, Machida, Japan, Sept. 12 and 13, 1986
8. A. Hay, Nature, 263 (1976) 538
9. G.G. Choudhry and O. Hutzinger, Mechanistic Aspects of the Thermal Formation of Halogenated Organic Compounds Including Polychlorinated Dibenzo-p-dioxins, Gordon and Breach, New York, 1983, p. 167
10. W.M. Shaub and W. Tsang, in R.E. Tucker, A.L. Young, and A.P. Grey (Editors), Human and Environmental Risks of Chlorinated Dioxins and Related Compounds, Plenum, New York, 1983, p. 731
11. W.M. Shaub and W. Tsang, Environ. Sci. Tech., 17 (1983) 721
12. W.M. Shaub and W. Tsang, in G. Choudhary, L.H. Keith and C. Rappe (Editors), Chlorinated Dioxins and Dibenzofurans in

the Total Environment II, Butterworth, Boston, 1985, p. 469

13. W. Sanderman, H. Stockman and R. Casten, Chem. Ber., 90 (1957) 690

14. G.A. Eiceman and H.O. Rghei, in G. Choudhary, L.H. Keith and C. Rappe (Editors), Chlorinated Dioxins and Dibenzofurans in the Total Environment II, Butterworth, Boston, 1985, p. 515

15. G.A. Eiceman and H.O. Rghei, Chemosph., 11 (1982) 833

16. H.O. Rghei and G.A. Eiceman, Chemosph., 13 (1984) 421

17. H.O. Rghie and G.A. Eiceman, Chemosph., 14 (1985) 167

18. G.A. Junk and J.J. Richard, in L.H. Keith (Editor), Identification and Analysis of Organic Pollutants in Air, Butterworth, Woburn, 1984, p. 63

19. L.C. Dickson and F.W. Karasek, Internat. J. Environ. Anal. Chem., 24 (1986) 55

Table I: Instrument Operating Parameters

Chromatographic Conditions

Fused Silica WCOT column 30m X 0.32mm I.D.

Stationary Phase DB-5, 0.25 um thickness

Helium carrier gas flow 2.5mL/min.

Temperature programs:

GC-ECD: 80°C for 1 min., to 300°C at 3°C/min., hold for 5 min.

GC-MS-EISIM: 80°C for 1 min., to 220°C at 20°C/min., to 300°C at 2°C/min., hold for 5 min.

Selected Ion Monitoring Mass Spectrometry

Ions	m/z	Dwell (ms)
TCDD	319.9, 321.9, 323.9	100
[$^{13}C_{12}$]-TCDD	267.9, 331.9, 333.9	100
P_5CDD	353.9, 355.9, 357.9	100
[$^{13}C_{12}$]-P_5CDD	301.9, 365.9, 367.9	100
H_6CDD	387.9, 389.9, 391.9	100
[$^{13}C_{12}$]-H_6CDD	335.9, 399.9, 401.9	100
H_7CDD	421.8, 423.8, 425.8	100
[$^{13}C_{12}$]-H_7CDD	369.8, 433.8, 435.8	100
OCDD	455.7, 457.7, 459.7	100
[$^{13}C_{12}$]-OCDD	405.7, 469.7, 471.7	100

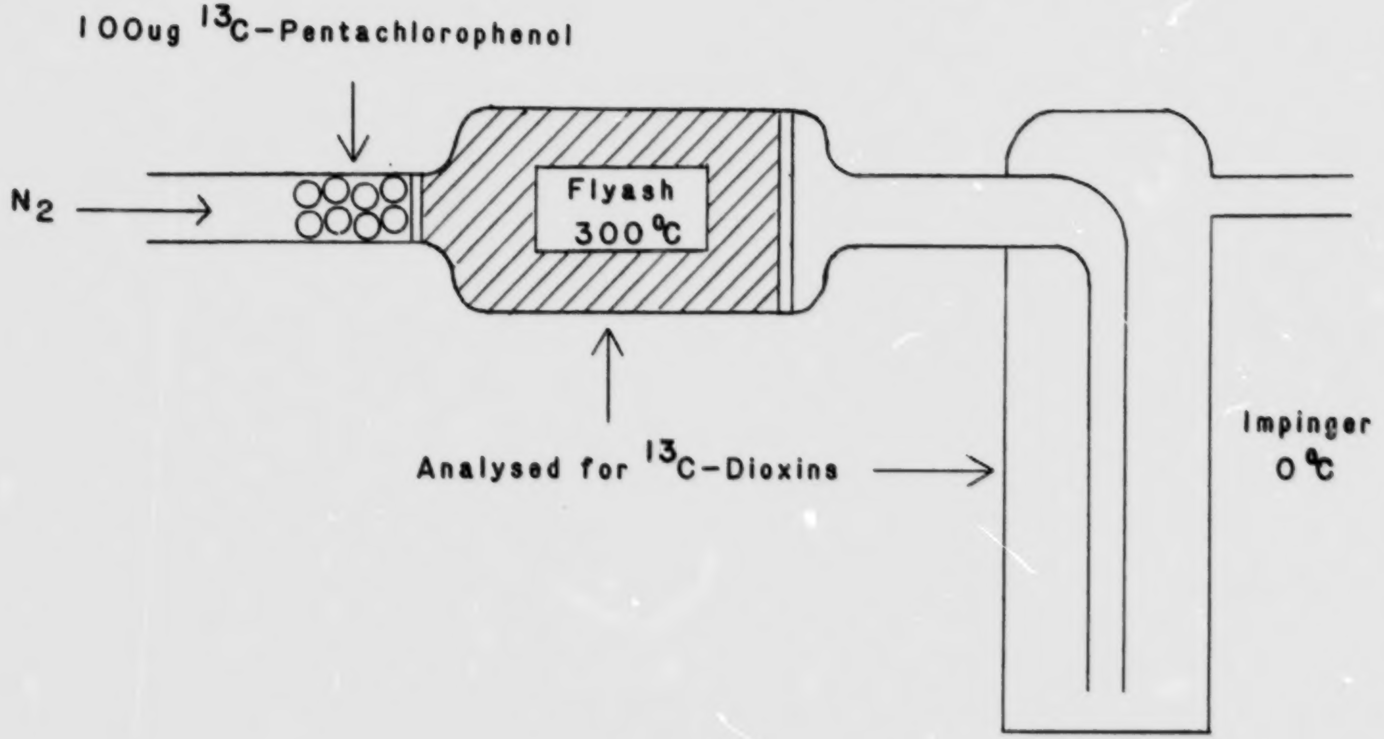

100ug ^{13}C-Pentachlorophenol
N_2
Flyash
300 °C
Analysed for ^{13}C-Dioxins
Impinger
0 °C

Figure 1: Schematic of Experimental Apparatus. Nitrogen flow carries chlorinated phenols through flyash bed and reaction products are collected downstream in the impinger and extracted from the flyash after the experiment.

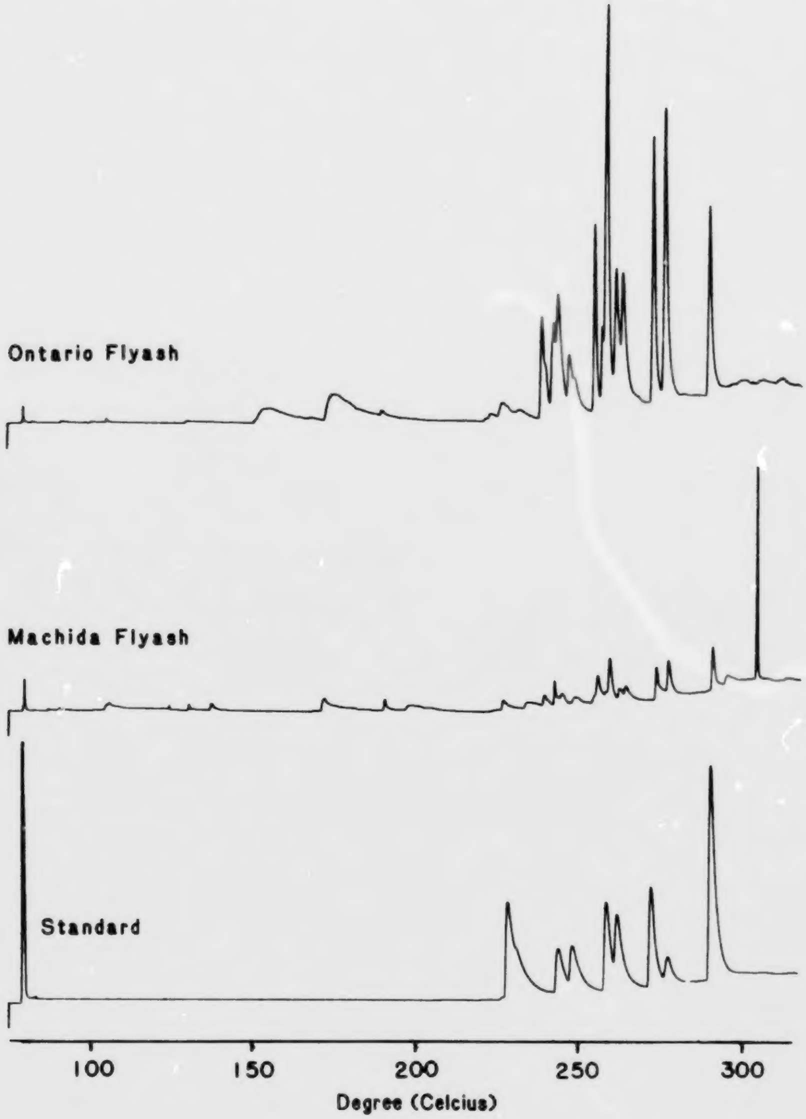


Figure 2: GC-ECD chromatograms of flyash extracts showing reaction products from ^{13}C-labelled pentachlorophenol.

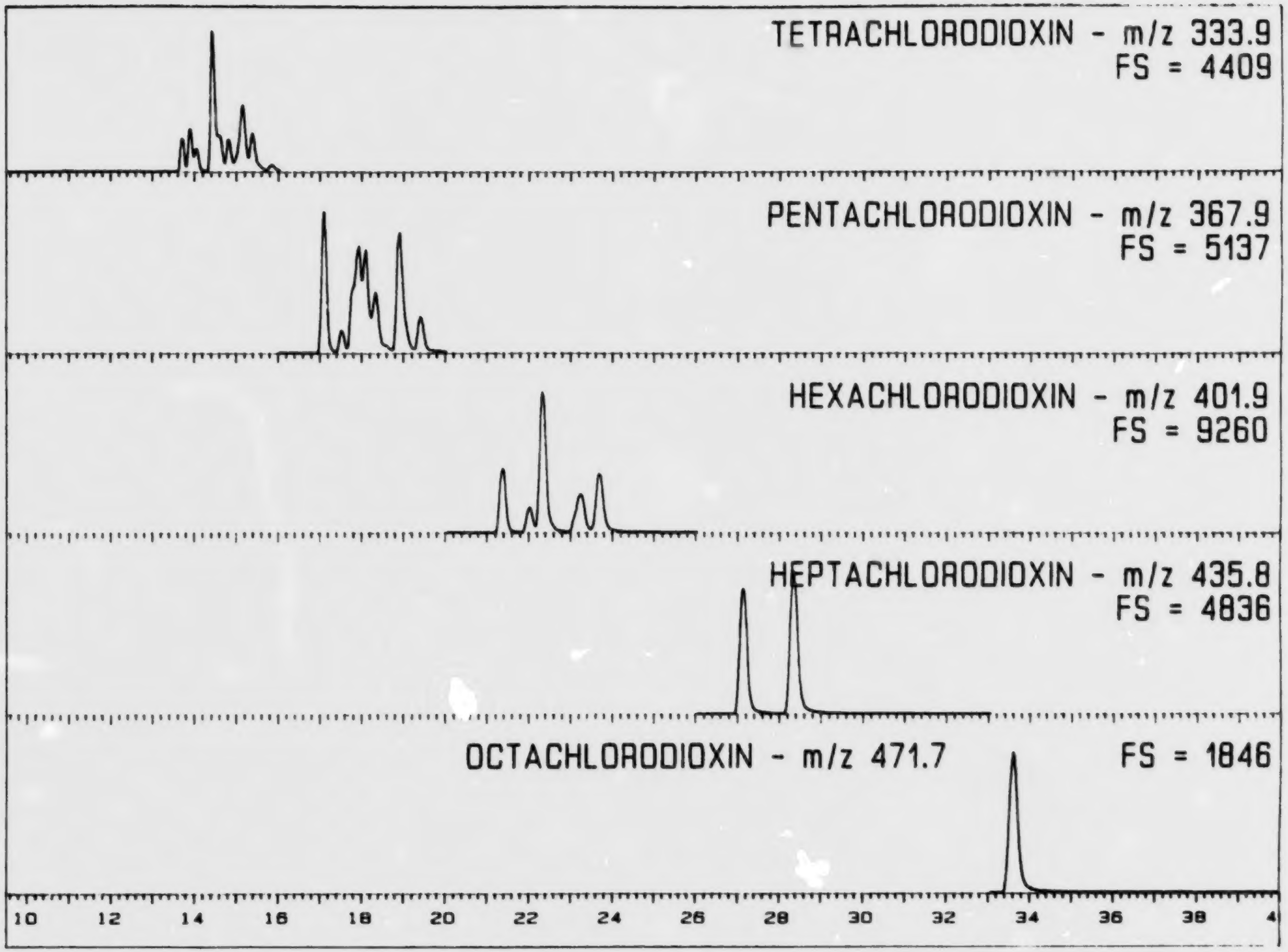


Figure 3: Chlorinated dioxins with ^{13}C produced from ^{13}C-pentachlorophenol using Ontario flyash. Each plot shows the abundance of the base peak of the dioxin congener versus retention time. The ion mass and the plot full scale are indicated at the right of each plot.

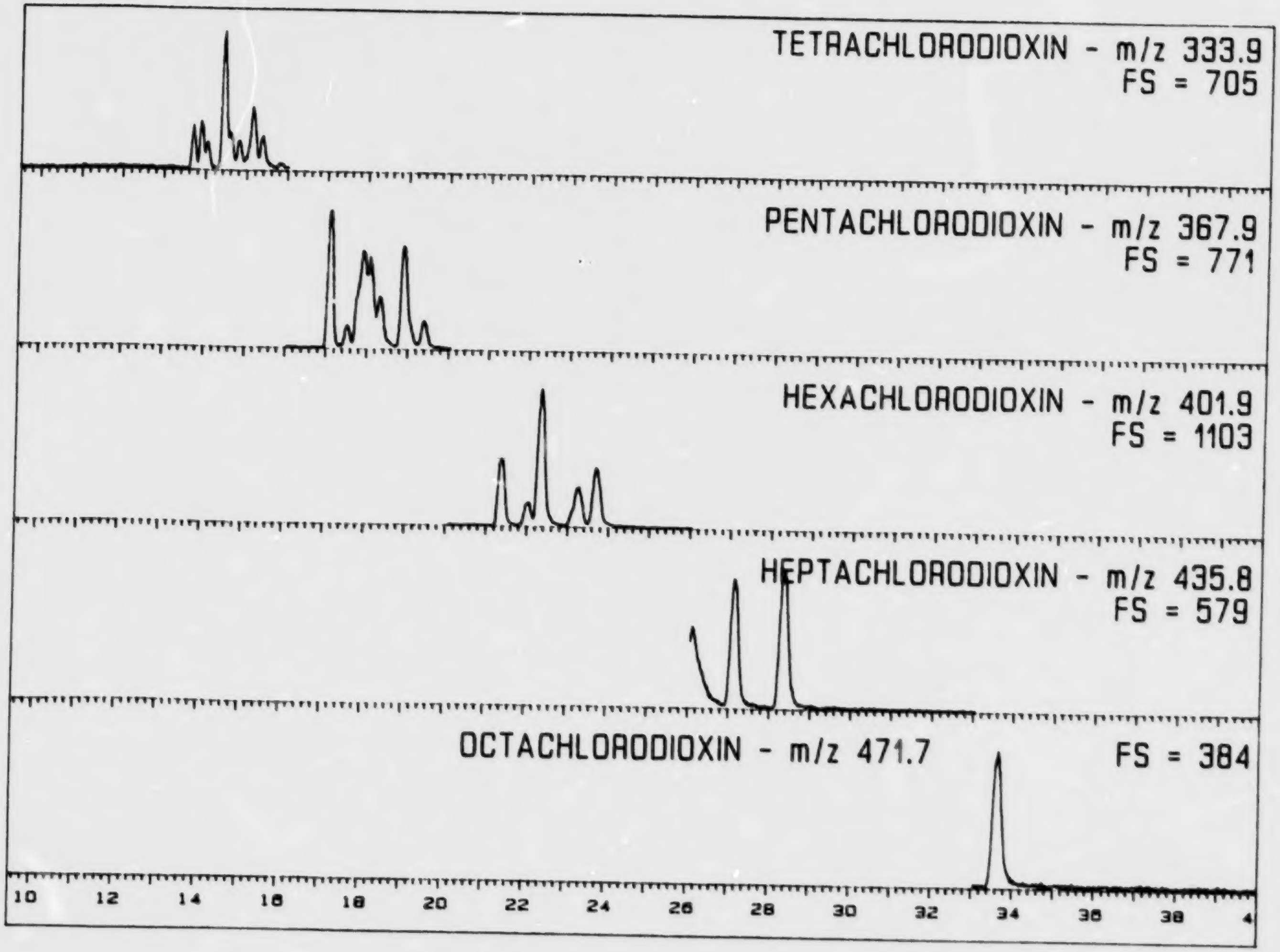


Figure 4: Chlorinated dioxins with ^{13}C produced from ^{13}C-pentachlorophenol using Machida flyash. Each plot shows the abundance of the base peak of the dioxin congener versus retention time. The ion mass and the plot full scale are indicated at the right of each plot.

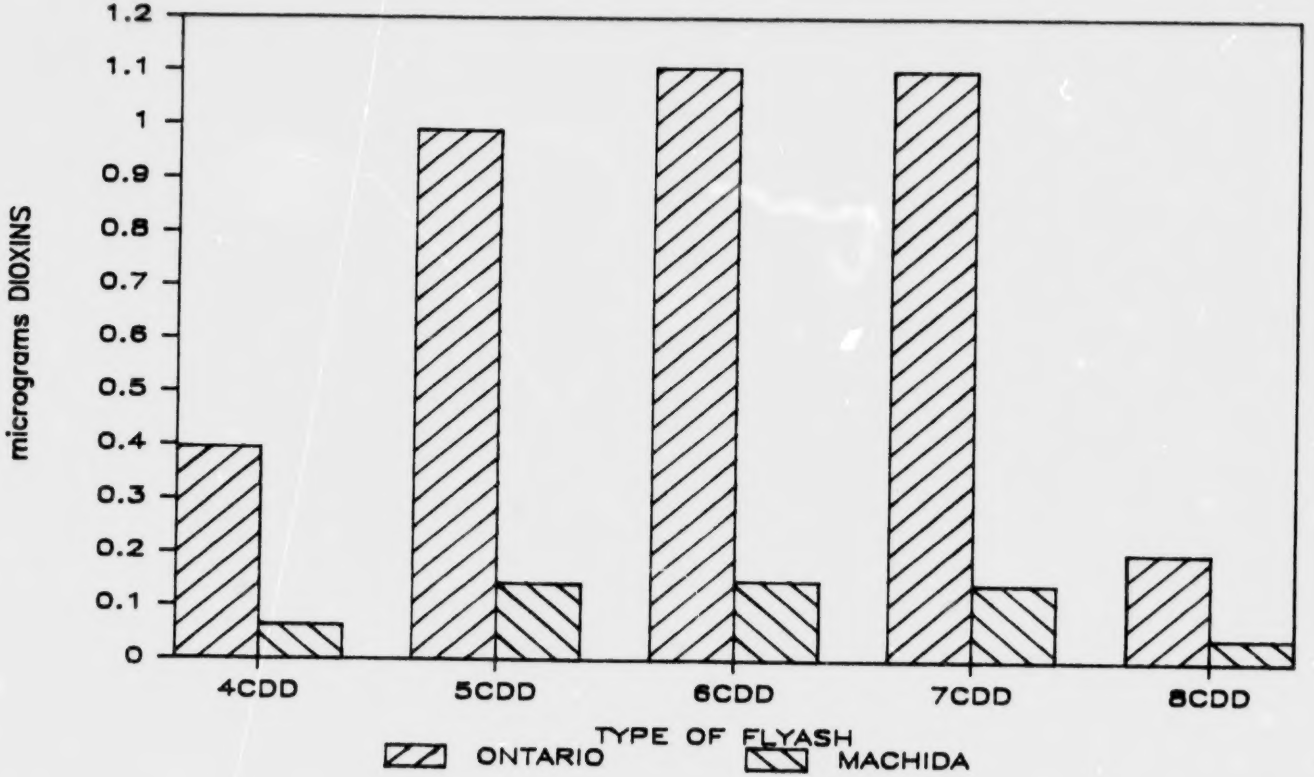


Figure 5: Bar chart showing the amounts of ^{13}C-labelled chlorinated dioxins formed from 100 micrograms of ^{13}C-pentachlorophenol using Ontario and Machida flyash. Over 3.2 micrograms of chlorinated dioxins were formed using Ontario flyash.

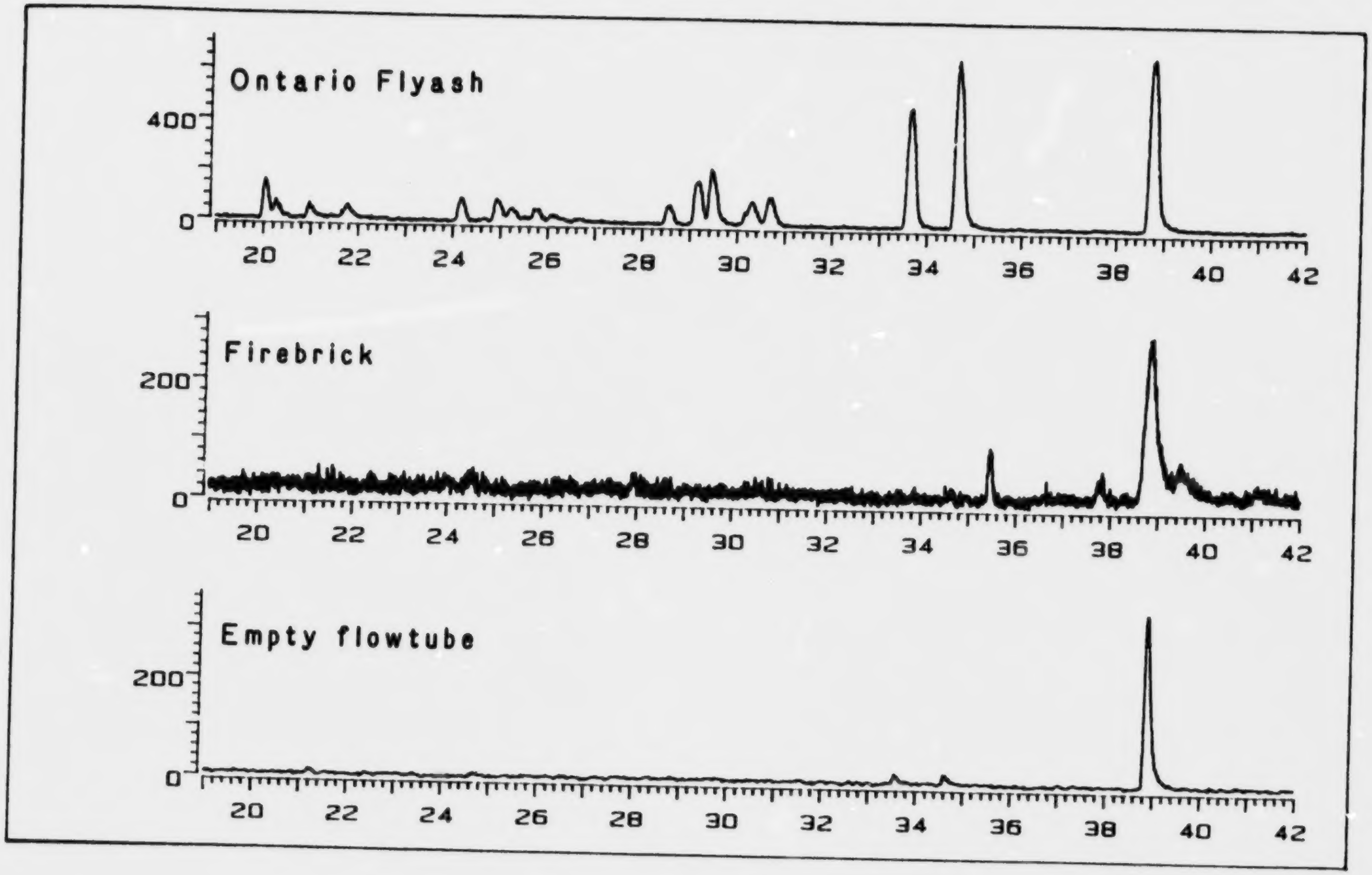


Figure 6: Chlorinated dioxins produced from pentachlorophenol using Ontario flyash, firebrick or an empty flowtube which were found in the downstream impinger rinses.

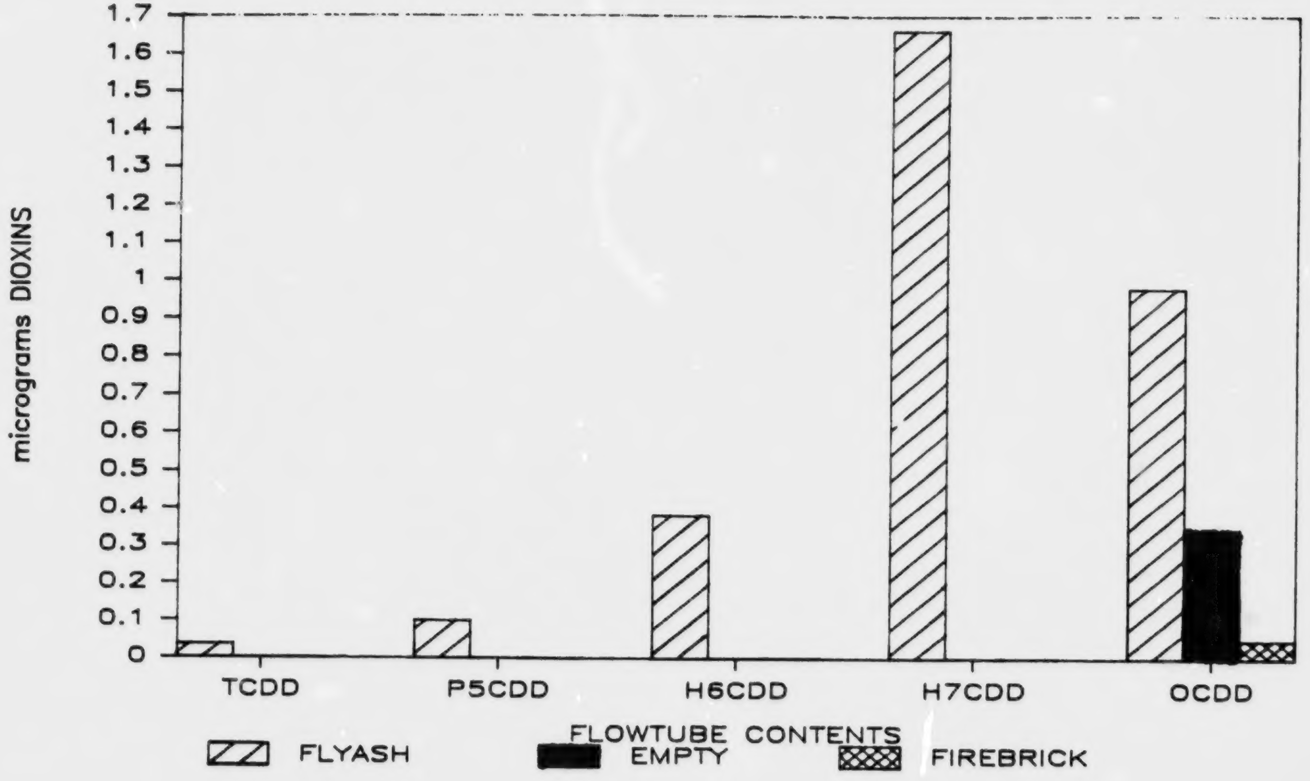


Figure 7: Bar chart comparing the amounts of chlorinated dioxin reaction products formed from 100 micrograms of pentachlorophenol using Ontario flyash, firebrick or an empty flowtube.

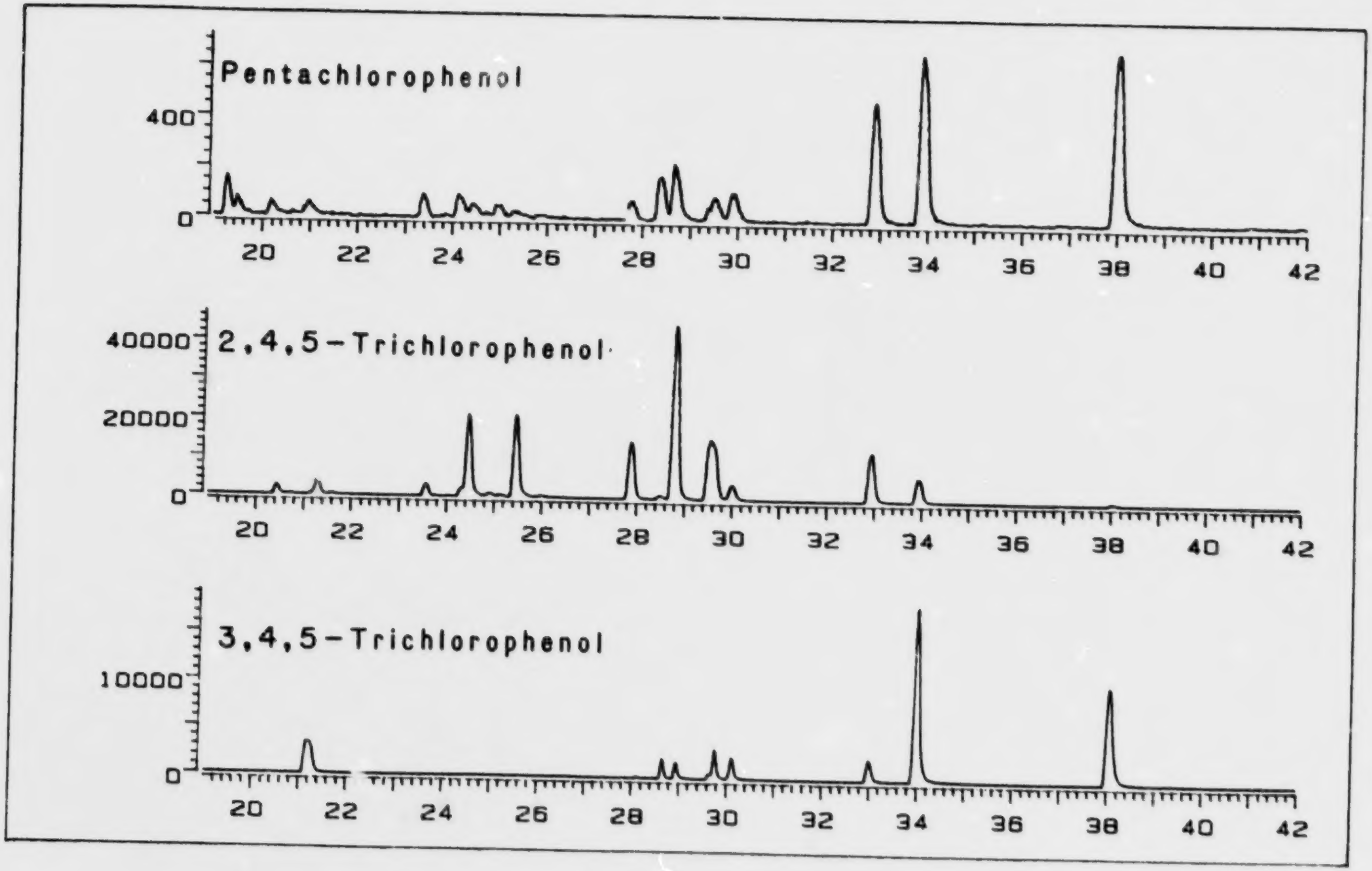


Figure 8: Chlorinated dioxin reaction products formed on Ontario flyash using from three different chlorinated phenols which were found in the downstream impinger rinses. The dioxin isomer distributions appear to be dependent upon the chlorine substitution pattern of the reactant.

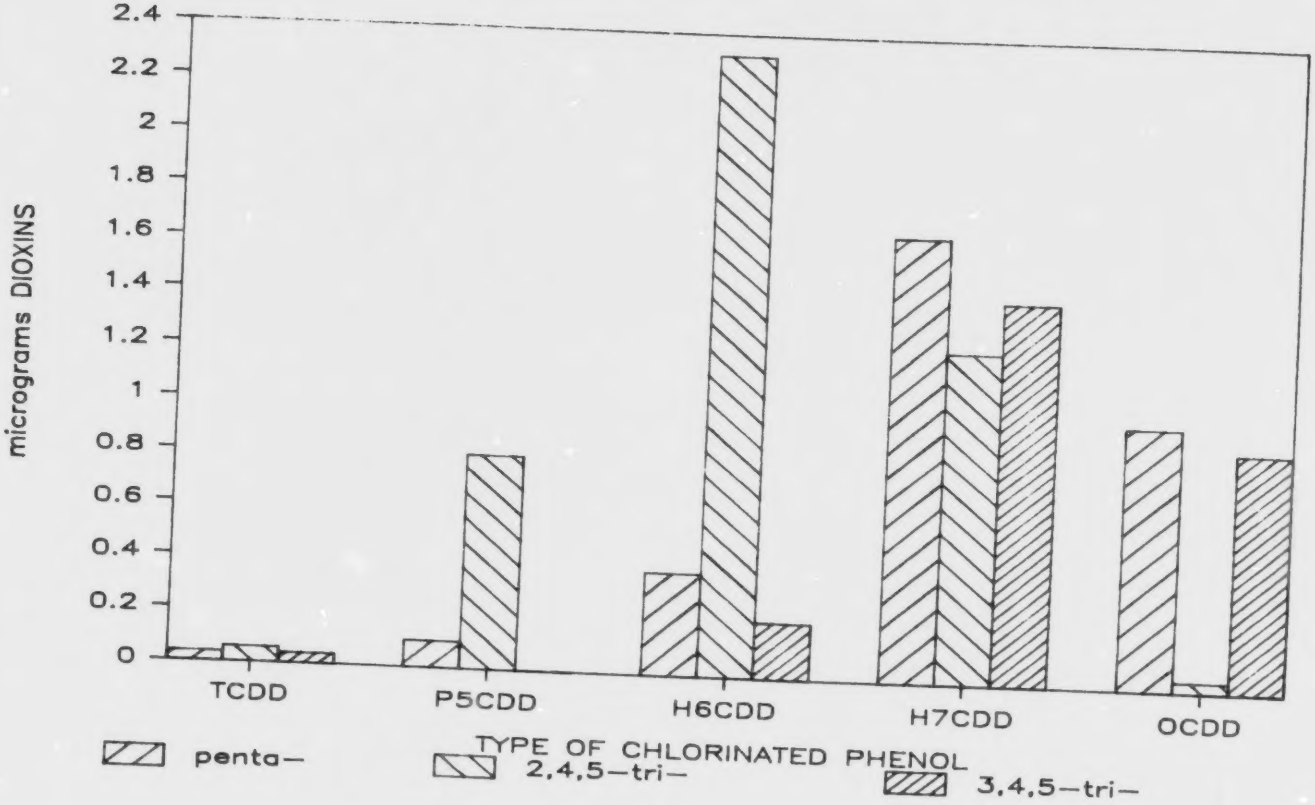


Figure 9: Bar chart comparing the amounts of chlorinated dioxin reaction products formed on Ontario flyash using three different chlorinated phenols.

TESTING OF A TOTAL HYDROCARBON MONITORING SYSTEM AT THE ASHBRIDGES BAY SEWAGE TREATMENT PLANT INCINERATOR, TORONTO.

J. Kosch, AMKO SYSTEMS, INC., Thornhill, Ontario

J. Marson, Ministry of the Environment, Toronto

INTRODUCTION

A continuous emission monitoring (CEM) demonstration at Toronto´s Ashbridges Bay sewage sludge incinerator was carried out. The project consisted of monitoring total hydrocarbon (THC) emissions for a period of 34 days and was carried out by AMKO Systems Inc.

The Ministry of the Environment´s (MOE) Source Assessment Unit (SAU) realized special interest in this project since problems have continued to hamper continuous emission monitoring (CEM) of THC in sludge incinerators. Continuous THC monitoring was mandatory in the Certificate of Approval of the Ashbridges Bay Plant.

The analyzer system installed on site in 1978 had only been functional for a few days. Fundamental design flaws such as insufficiently heated sample-wetted lines and detector in the Horiba analyzer were the cause of this negligible performance. The developments and testing of a quasi maintenance-free monitoring system was found necessary in view of the many problems existing in CEM THC installations.

Plant Management at Ashbridges Bay was contacted and very receptive to our finding a cure for its inoperative THC monitoring system.

The objectives of this study were 1) to design a Flame Ionization Detector (FID) based THC monitoring system, complying with MOE guidelines, that was capable of extended up-time by application of an efficient sample conditioning system and 2) to operate a THC analyzer for a period of 30 days so as to assess CEM up-time, accuracy and maintenance requirements.

SUMMARY

A total hydrocarbon emission monitoring system was successfully demonstrated at the Ashbridges Bay sewage sludge incinerator stack. The system was at the stack for 34 days and produced valid data for 67% of the time. Most of the down-time was due to chart recorder problems. Had more appropriate funding been made available for daily inspection, 95% up-time would have been realized. During the 546 hours of valid data, the stack gas concentrations averaged 720 ppm, as methane, and the daily averages ranged from 432 ppm to 1229 ppm. These values are in line with previous measurements (1982). The cause of the high THC concentration has not been determined in this work.

PROCESS DESCRIPTION

Our tests were conducted at the main stack of the Ashbridges Bay sewage treatment plant. The stack vents a number of sludge incinerators with combined throughput of an estimated 13.5 tons of dry solids per hour. The stack gas flow is approximately 32m3/sec. During the program there were typically four units in operation. The incinerators are multiple hearth type and combustion is supported with natural gas fuel. The exhaust gases from each incinerator are cleaned in separate water scrubbers before entering the common stack. The approximate composition of the stack gases is as follows:

CO_2 : 2.6%
O_2 : 15.0%
CO : 0.5%
N_2 : 81.9%
Moisture : 6.5%
Particulate : 10 mg/m3
Temperature : 33 degress C

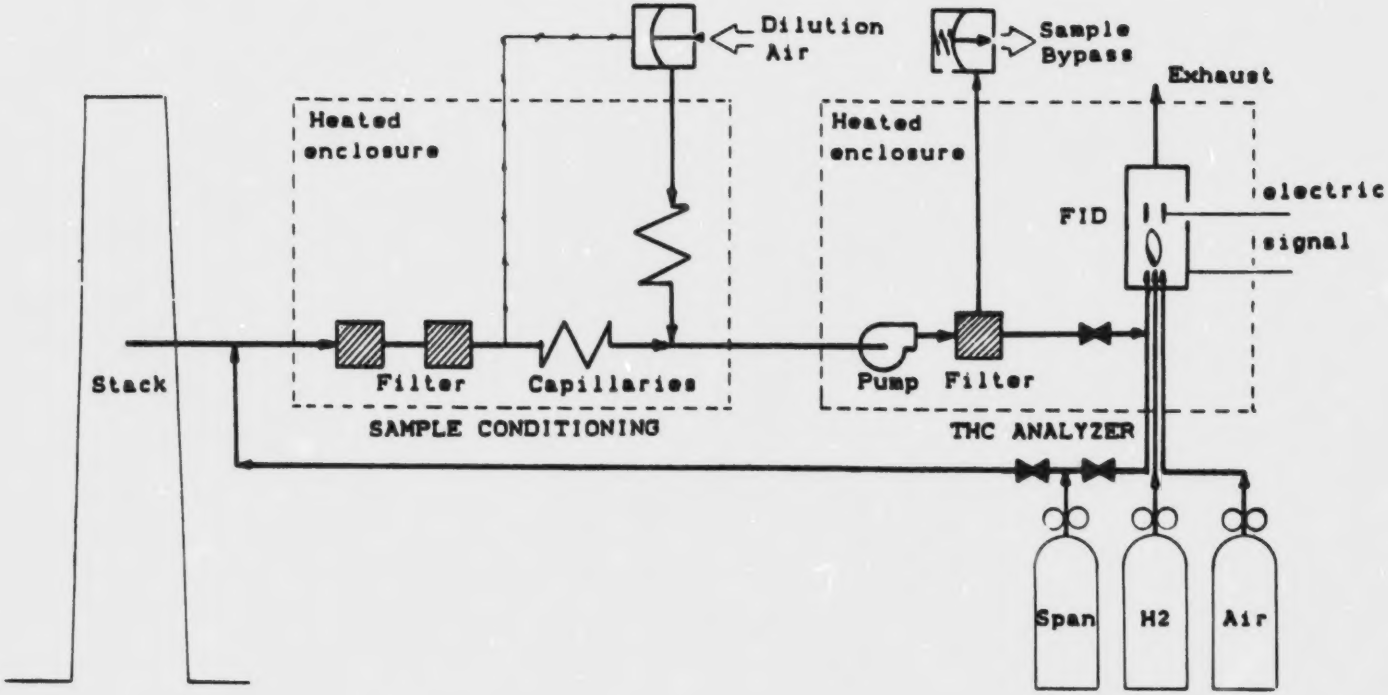
The sampling location is at the 64m elevation of the 183m main stack. The sampling platform is enclosed between the stack liner and the concrete shell, accessible by elevator.

OUTLINE OF THE MONITORING SYSTEM

The THC monitoring system consisted of a probe, a sample conditioning unit and a THC analyzer. The monitor´s fuel, fuel-air and span gas cylinders were housed in a ground cabinet, adjacent to the stack, and connected to the analyzer via one-quarter inch stainless steel tube. The probe was three meters long and made of one-half inch stainless steel pipe. Our enclosed sample conditioning unit consisted of two filters followed by a dilution system. The analyzer was a Ratfisch RS5 (1974) which is equipped with an FID. The THC monitoring system is depicted schematically in Figure 1.

The stack gas sample was extracted at the rate of about one liter per minute. Particulate matter was removed by coarse and fine filters. The filtering elements were 1" x 2 1/2 " Balston cylinders with efficiency for 0.1 micron particles rated at 93% and 99.99%, respectively. Sample conditioning included a 1.1 sample dilution stage. Dilution was accomplished by throttling the sample flow (11/min.) with a 30 cm long, 1/8 inch OD tubing coil. A similar coil was used to throttle the flow of dilution air (11/min.). The inlet pressures of the two capillaries were matched by a modified pressure regulator. The filters and capillaries were maintained at 150 degress C.

FIGURE 1
THC SYSTEM SCHEMATIC



The Ratfisch total hydrocarbon analyzer was adjacent to the conditioning module. The analyzer was a heated type and the sample path temperature was maintained at 160 degress C. The sample flow to the detector was about 50 ml/min. and the rest of the sample was bypassed. The monitor´s range was set at 1000 ppm and the span gas was 225 ppm methane in nitrogen. This span gas was later on replaced by 545 ppm methane in nitrogen so as to approach the more typical THC ranges observed in this study. The span gas was injected either at the analyzer or at the probe. In the first case, the gas was used to calibrate the instrument, whereas in the second case, it served to verify the operation of the sample conditioning system.

The THC measurements were registered on a potentiometric strip chart recorder with problematic Z-fold feed.

RESULTS AND DISCUSSION

The THC system was installed on April 10, 1985 and remained on site for the next 34 days. The system was inspected daily during the first week of operation and every three to four days thereafter. The inspection consisted of the following:

a) verification of dilution system and analyzer temperatures
b) checking the zero and span values
c) checking sample back pressure
d) recalibrating the analyzer
e) checking dilution ratio by feeding span gas at the sample probe.

Maintenance was limited to changing the coarse particulate filter after 25 days of operation. However, the thermostat of the THC analyzer was repaired during the test period, resulting in 48 hrs of lost data. Another 24 hours were lost when the cylinder ran out of fuel-air. Additional data losses resulted from jammed chart paper.

In total, the THC system produced 545 hours of valid data. The operating record of the system is summarized in Table 1.

Table 1
THC SYSTEM OPERATING RECORD

Valid measurement records	546 hrs (67%)
Chart recorder malfunction	166 hrs (20%)
Analyzer malfunction & repair	48 hrs (6%)
Calibration	24 hrs (3%)
Out of compressed air	24 hrs (3%)
Maintenance	8 hrs (1%)
TOTAL	816 hrs (100%)

The hydrocarbon concentrations values averaged 720 ppm and the daily averages ranged from 432 ppm to 1229 ppm. No attempt was made to relate these THC concentrations with incinerator operating conditions. The 720 ppm average is close to the 698 ppm average measured at this site in April of 1982 and significantly higher than previously recorded in May of 1979 (200-400 ppm).

The THC measurements are summarized in Table 2.

Table 2
THC MEASUREMENTS SUMMARY

DATE	MEAS. HOURS	THC PPM AVE.	STD. DEV.
April 11	9	465	84
April 12	24	435	172
April 13	24	688	285
Arpil 14	24	577	128
April 15	24	791	450
April 16	22	932	300
April 17	22	785	329
April 18	22	574	190
April 21	12	533	198
April 22	24	473	68
April 23	22	619	126
April 24	24	1035	142
April 25	23	868	127
April 26	24	1006	164
April 27	22	1273	260
April 28	24	1229	461
April 29	23	689	182
April 30	23	734	162
May 1	7	432	110
May 8	11	659	77
May 9	24	948	134
May 10	24	688	51
May 11	24	465	113
May 12	24	634	122
May 13	24	579	92
May 14	15	618	46
TOTAL	545	-	-
AVERAGE	20.9	720	176

The analyzer zero drift was less than 10 ppm and the span drift was negligible.

The dilution factor of the sampling conditioner was checked several times during the testing period. The dilution factor averaged 0.53 and ranged from 0.50 to 0.55, with one exception. The exception (dilution factor =0.70) was probably due to improper FID setting.

The average solution factor was the perimeter used to calculate the Table 1 concentrations. The dilution factor verifications are listed in Table 3.

Table 3
DILUTION FACTOR VERIFICATIONS

DATE	DILUTION FACTOR
April 13, 1985	0.53
April 14, 1985	0.54
April 15, 1985	0.50
April 16, 1985	0.51
April 17, 1985	0.53
April 18, 1985	0.52
April 21, 1985	0.55
April 23, 1985	0.50
April 25, 1985	0.50
April 26, 1985	0.70*
April 28, 1985	0.54
April 30, 1985	0.54
May 7, 1985	0.52
May 8, 1985	0.51
May 14, 1985	0.50
AVERAGE	0.53

*Recalibration made fuel-air setting too sensitive.

$$\text{Dil.factor} = \frac{\text{Meas. of span gas injected at the probe}}{\text{Meas. of span gas injected at the analyzer}}$$

CONCLUSIONS

1. The feasability of monitoring hydrocarbon emissions at this site was demonstrated. The maintenance requirements of a THC system equipped with an adequate sample conditioner are in line with other types of continuous monitoring systems.

2. The THC monitoring system produced 546 hours of valid data (67% up-time). Unavoidable data losses, resulting from analyzer calibration, maintenance and repair, totalled 10%. Data losses caused by recorder malfunction and insufficient air supply totalled 23%, and may have been easily avoided with in-plant maintenance.

3. The hydrocarbon concentration measurements averaged 720 ppm and the daily averages ranged from 432 ppm to 1229 ppm. Some process modifications were implemented since these tests and their effect will be subject to further testing.

The co-operation between the MOE´s Source Assessment Unit and AMKO Systems Inc., has been of significant value in demonstrating the ease of obtaining valid continuous THC data from a sludge incinerator. For the first time in seven years at this site, continuous hydrocarbon emission data was realized. The success of this project was based on 1) design of an appropriate sample system and 2) an FID THC analyzer designed for this type of operation. With additional funding, daily inspection could have easily resulted in 95% up-time. It must be noted that this study has benefited AMKO by extending its application-base into this priority area while resolving a question that needed to be addressed for years.

STUDY OF THE SPATIAL DISTRIBUTION OF THE IMPACT OF SUDBURY SMELTING EMISSIONS

J.M. Byrne, E.A. McBean, J. Donald and G.J. Farquhar

Department of Civil Engineering
University of Waterloo
Waterloo, Ontario, Canada N2L 3G1

ABSTRACT

The two mining and smelting operations near Sudbury, Ontario are the source of greater than half of the total SO_2 emissions in Ontario (Tang et al., 1984). These releases are examined to improve the understanding of the resulting areal deposition patterns. The intent of this focus is threefold:

(i) to develop contouring procedures which will allow generalization of point-specific measured information, and to indicate regions that would be impacted by various levels of remedial control technologies;

(ii) to better understand the long term deposition levels, reflecting meteorologic variability on annual and seasonal levels; and

(iii) to compare with monitoring station records to observe whether additional and/or fewer monitoring stations may be appropriate.

1. INTRODUCTION

This paper is a review of some of the acid rain research going on at the University of Waterloo under funding from the Ontario Ministry of the Environment and the National Scientific and Engineering Research Council. The specific focus of the Ministry funding is a two part study of the Acid Precipitation in Ontario (APIOS) Air and Precipitation chemistry network. Phase I is directed at the spatial definition of the impacts of SO_2 emissions from the INCO and Falconbridge smelters at Sudbury. The second phase will utilize the North American source inventory (ie. 253 point sources and 83 areal sources) in a detailed analysis of the spatial resolution provided by the APIOS network. It is felt that this work will provide useful informattion regarding the capability of the APIOS network to:

(a) accurately reflect the true spatial pattern of acid deposition over much of Ontario;

(b) identify significant changes in emissions at major sources within an established time period.

A significant portion of the work involves the development of an accurate spatial analysis technique for characterizing acid deposition patterns. Kriging, a spatial interpolation method that minimizes the interpolative error, and provides an estimate of that error, is being utilized as the tool for integrating discrete data points to a spatial field. However, the application of kriging techniques to large geographic areas is subject to error due to the distortion in projecting a spherical surface onto a square grid. Development of a modified kriging method, employing transforms of lattitude and longitude to a square grid for kriging analysis is ongoing at this time.

2. BACKGROUND

The two mining and smelting operations near Sudbury are the source of greater than half of the total SO_2 emissions in Ontario (Tang et al., 1984). Scientists had generally assumed the major environmental impact of Sudbury emissions was upon the immediate area of Northern Ontario. This assumption was accepted because deposition amounts in Sudbury were high, and it was logical to attribute the deposition to the nearby, large emission sources. However, this has been shown to not be the case. Chan et al. (1984) and Tang et al. (1984) studied deposition variability near Sudbury and throughout Ontario. Using deposition and air concentration data, and sector stratification techniques, Chan et al. concluded that very little of the sulfur compounds emitted at Sudbury are deposited close to the source (within 40 km.). Most of the deposition in this area was attributed to upwind sources. Tang et al. utilized extensive periods of smelter shutdown during 1982 and 1983 to demonstrate the upper limit of Sudbury contributions to deposition at six Ontario stations ranged from two to forty seven percent. These studies demonstrated two points:

1. most of the acid deposition around Sudbury is due to pollutants transported into the area from other sources; and
2. most of the Sudbury emissions are deposited outside of the Sudbury area.

The analysis of Sudbury emission deposition patterns to be presented below, utilize the UW-LRT Model. The model is a modified version of the Ministry LRT statistical model (Venkatram et al., 1982). Shipley (1986) modified the original model to include trajectory analysis routines in the calculation of the transfer coefficients. The dispersion function was refined further to include variable wind speed and the resultant variation in dispersion (Byrne et al., 1986). A comparison of model results to output from the more complex AES LRT model (Olson and Voldner, 1981) demonstrates the UW-LRT model is a practical, although simpler and more approximate, alternative that may be used to address certain questions.

3. RESEARCH PROCEDURES

In this study, the focus is on the impact of Sudbury emissions. To accomplish the objectives of this work, the following steps have been carried out:

1. Statistics on wind variability from season to season have been compiled as input for UW-LRT simulations;

2. the Sudbury impacts on eastern North America were generated;

3. Mapping of impacts - the model-defined spatial patterns will be utilized in concert with kriging techniques to define the actual area impacted by Sudbury emissions, and the variation of the impacts within that area.

The intent of this analysis is threefold:

(i) to provide generalized information regarding the improvement in environmental quality in regions impacted;

(ii) long-term impacts, reflecting meteorologic variability, will be determined. Our intent is to examine the contours arising from years for which there are recorded deposition data, the "average" year, and its associated distribution.

(iii)the deposition patterns will be compared with the monitoring stations to observe whether additional and/or fewer stations are appropriate. Several alternative tests will be utilized to determine the information returns for changes in the number of stations in the APIOS network.

It should be noted that the above pertains principally to the impacts of Sudbury. We have included in Part I only this source to assist in development of the methodology and to explore the effect of alternative approaches to contouring. In Phase II, the information will be generalized to other sources. It is only after Phase II that an assessment of the entire APIOS network will be complete.

4. UW-LRT MODEL

The University of Waterloo LRT Model combines a statistical trajectory routine (Shipley, 1986) with a dispersion function adapted from Ellenton et al. (1985) and a mass balance scavenging function developed by Venkatram et al. (1982). The trajectory routine utilizes wind direction and speed statistics compiled from analyzed, six hourly, upper air trajectory fields at the 850 mbar constant pressure surface. Output from the model consists of source-receptor deposition linkages (transfer coefficients). For the simulations presented here, the 1980 emission inventory for eastern North America was used for all years. The inventory contains 318 SO_2 sources, of which 235 are point sources and the remaining are areal sources. The emission sources were matched to the nearest of 120 wind data grid points. Multiple sources at a common grid point were summed, and treated as a single source located at an emission-weighted mean lattitude and longitude. There was no combining of point and areal sources. The end result was a pooled network of 45 point sources and 29 areal sources, for a total of 74 pollutant sources. Model simulations were run for receptor grid of 192 points over eastern North America. Modelled spatial patterns were drawn using standard contouring packages.

5. RECOGNITION OF EMISSION REDUCTION

A key question for managers of acid deposition monitoring networks involves the ability of the network to recognize a change in deposition levels due to discrete changes in emissions at a major source(s). Efforts to improve deposition pattern resolution involves detailed network design and station siting criteria, and well defined collection, storage and analysis techniques. However, minimization of system errors, while necessary, does not address the natural variability in acid deposition due to atmospheric processes (wind speed and direction, mixing height, precipitation, chemistry, etc.). Attempts to define the relative impact of the parameters contributing to acid deposition variability are ongoing. The opinion here is that system error is small compared to the true spatial variation in acid deposition. This view is supported in the literature (Granat, 1975). In order to recognize a change in deposition that is directly related to emission reduction, one must first be capable of manipulating the data to minimize, to a reasonable degree, the variation due to the physical processes. At that point, the principal parameter affecting deposition would be the emission variation.

The ongoing analysis of variation in wet sulfur deposition at UW theorizes that three components contribute most of the variability in acid deposition. These are: transport phenomena (ie wind trajectory and speed); deposition phenomena (principally spatial and temporal precipitation patterns); and emission variation. The UW-LRT model is felt to reflects elements of the transport phenomena and its associated variability. The effect of precipitation spatial patterns is currently being examined, for eventual comparison to analyzed spatial deposition fields. However, analysis of the rainfall and deposition fields will not be completed until the distance transform routines have been verified.

Several studies (Chan et al., 1982; Tang and Chan, 1985) have attempted to define the regional impact of Sudbury emissions by comparing deposition data collected during extensive smelter shutdowns to data collected during normal operations. These studies found a high degree of deposition variability, but with careful analyses, they were able to establish that most of the deposition of wet sulfur in the Sudbury area is due to emission from other sources. Of interest in this study is to determine the extent to which adjustments of the two data sets (operational and non-operational) to minimize other forms of variability would improve the understanding of the deposition patterns. The following discussion demonstrates how LRT variability effected the Sudbury area deposition during the shutdown period.

The INCO and Falconbridge smelters contribute 812 and 123 k tonnes of SO_2, respectively, to the emission levels at Sudbury. Both plants were shut down (with minor exceptions) from July, 1982 to January, 1983, and INCO remained shutdown for the first quarter of 1983. Figures 1, 2 and 3 are UW-LRT simulations of wet SO_4 deposition for the summer (July - September), and fall (October - December), 1982, and the winter (January - March), 1983. A background level of 1.5 kg. SO_4 / ha is included. The simulated patterns assume all sources emitted at 1980 levels, therefore, emission variability is nil. This assumption is the only possible approach since emission inventories do not exist for other years. The contours reflect the deposition that would have occurred, given the variability in trajectory statistics for each quarter. Examination of the figures indicates the deposition rate is greatest in summer and smallest in winter. This is not unexpected, given the model incorporates the effects of transport winds. Typical summer conditions in eastern North America involve slow air movements associated with stagnant high pressure cells of a sub-continental scale. Dispersion is less effective with low wind velocities, and pollutant concentrations would tend to increase to higher levels. Winter conditions involve frequent storms associated with the intensified westerly flow that dominates weather conditions. Wind levels are generally higher; consequently, pollutants are dispersed quickly, and transported out of the deposition area in less time. The Fall of 1982 (Figure 13) represents a transition phase.

Figures 4, 5 and 6 provide estimates of the magnitude of deposition change that may be expected due to the Sudbury shutdown. For example, for Summer 1982, the net effect on the APIOS network would have been in the range of 0.6 to 1.4 kg. SO_4 / ha. These small, net values would be very difficult to recognize in a deposition field with a high variation, which is in fact, the case.

Simulations of the eastern North American deposition for the shutdown seasons are provided in Figures 7, 8 and 9. These figures are identical to Figures 1, 2 and

3 except that the Sudbury emissions were set to 0. Preliminary comparisons of the figures reveals little. However, overlay comparison demonstrates a definite and significant shift in the isopleths as a direct response to Sudbury emissions. Figure 10 demonstrates this shift for three prominent contours. The change, though undeniable, is likely not statistically significant. Current efforts are being directed at defining statistical measures that will detect this type of variation. However, development of a suitable test for recorded data is dependent on the development of an accurate kriging routine, together with the associated projection transforms.

6. MULTI-YEAR WIND VARIABILITIES AND DETECTION OF SUDBURY SHUTDOWNS

Attempts to compare the deposition recorded during smelter shutdown periods with periods of operation are based on the assumption that the deposition is strongly related to emission levels. This is true for the macro scale only. The impact of individual sources on receptors within a reasonable proximity may not be sufficient to outweigh the variation due to other factors. The following example illustrates this phenomena. The UW-LRT model was used to simulate the quarterly depositions for the years 1980 through 1984. The deposition patterns reflect the wind speed and direction variability for each season. Therefore, the variation in location of any isopleth over the total period (for any season) reflects the deposition variability due to wind variation. Figures 11, 12 and 13 present this variation for an equivalent contour for the summer, winter and fall seasons, respectively. Consider Figure 11; in Summer 1982, one expects the deposition in the Sudbury area to be lower due to the shutdown. However, the location of the 6 kg isopleth indicates that deposition would have increased in lattitude from "average" conditions because the wind conditions have effectively shifted the sub-continental deposition pattern northward. This change should be accounted for in attempts to identify deposition reductions due to the shutdown. The shutdown and deposition shift effectively 'cancelled' one another. This effect is even more pronounced for winter, 1983 (Figure 12), where the 4.5 kg contour is much further north than those of other years.

7. CONCLUSIONS AND FUTURE WORK

Analyses of the principal factors contributing to variability in acid deposition are ongoing. A LRT Model that reflects transport variability has been developed. Spatial analysis techniques to analyse rainfall and deposition patterns are currently under development. The rainfall spatial patterns will be utilized to determine the net effect of rainfall variation on acid deposition. Refining of the analysis will be carried out while defining the spatial patterns attributable to Sudbury emissions. Phase II will involve applying the analysis to the North American situation, with a specific intent of determining the current and potential sensitivity of the APIOS network to changes in acidic emissions.

8. ACKNOWLEDGEMENTS

The authors wish to thank Maris Lusis, Walter Chan and Al Tang of the Air Resources Branch for valued input. Marvin Olson, AES Canada, kindly provided the wind field data used in this study.

REFERENCES

Byrne, J.M., E.A. McBean, K.B. Shipley and G.J. Farquhar. 1987. Simulation of Wet Sulfate Deposition in Eastern North America. Manuscript submitted to TELLUS.

Chan, W.H., R.S. Vet, Chul-Un Ro, A.J.S. Tang and M.A. Lusis, 1984. Atmospheric Environment, 19,1001-1008.

Ellenton, G., B. Ley and P.K. Misra, 1985. Atmospheric Environment, 19, 727-737.

Granat, L. 1975. Principles of Network Design for Precipitation Chemistry Networks. University of Stockholm, Sweden.

Olson, M.P. and E. C. Voldner, 1981. Documentation of the AES-LRT Air Pollutants Model. Report for Atmospheric Modeling Subgroup of Work Group 2, Phase II. MOI on Transboundary Air Pollution.

Shipley, K.B., E.A. McBean, G.J. Farquhar and J.M. Byrne, 1987. Incorporation of Wind Roses in a Statistical Long Range Transport Model. Under review by Water, Air and Soil Pollution.

Tang, A.J.S., W.H. Chan and M.A. Lusis, 1984. An Analysis of the Effects of the Sudbury Emission Sources on Wet and Dry Deposition in Ontario. OMOE-ARB-124-84-ARSP.

Venkatram, A., B.E. Ley and S.Y. Wong, 1982. Atmospheric Environment, 16, 249-257.

Figure 1 SPATIAL DEPOSITION - SUMMER 1982. 74 SOURCES

UW - LRT SIMULATION

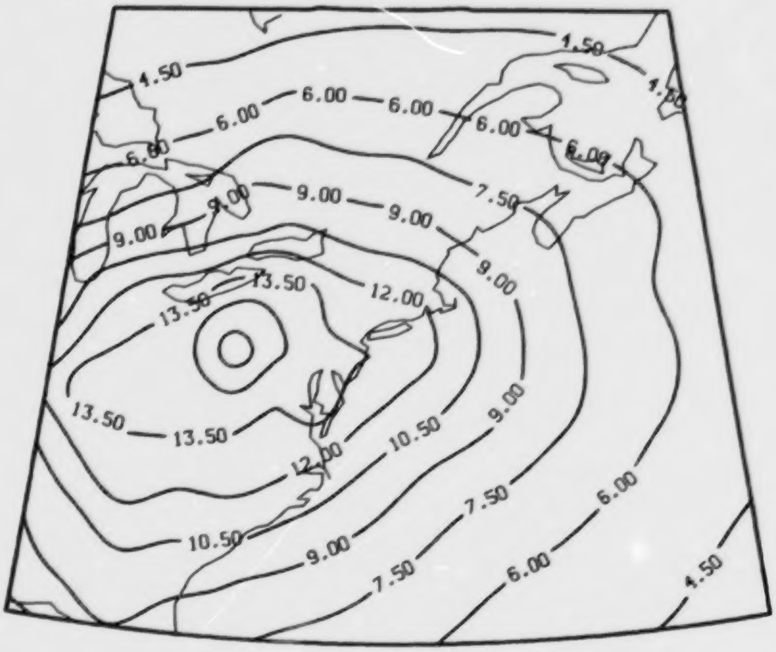


Figure 2 SPATIAL DEPOSITION - FALL 1982. 74 SOURCES

UW - LRT SIMULATION

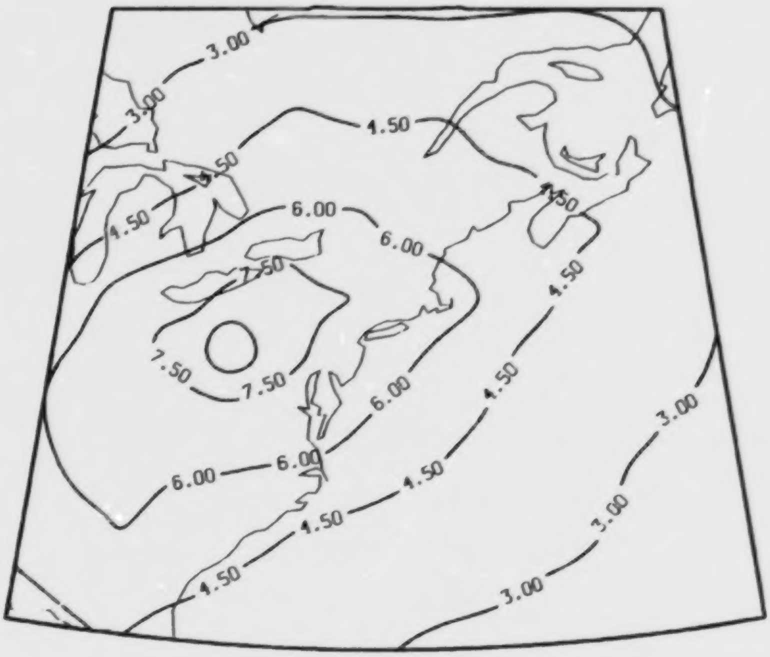
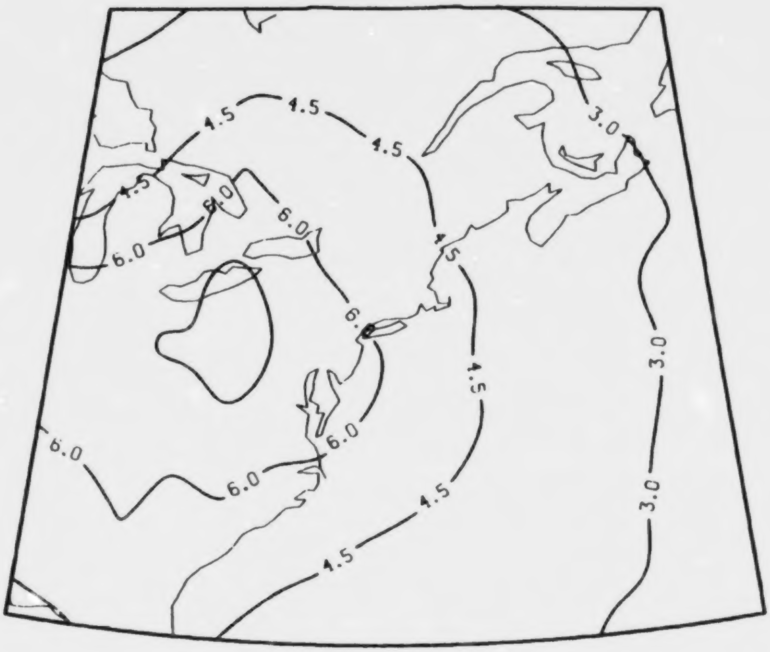


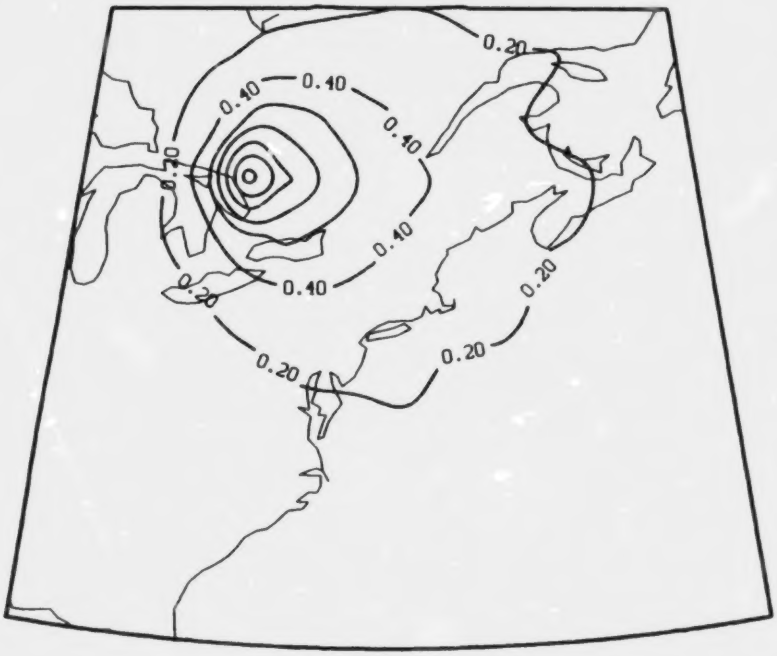
Figure 3 SPATIAL DEPOSITION - WINTER 1983. 74 SOURCES

UW - LRT SIMULATION



SPATIAL DEPOSITION - SUMMER 1982. SUDBURY SOURCE

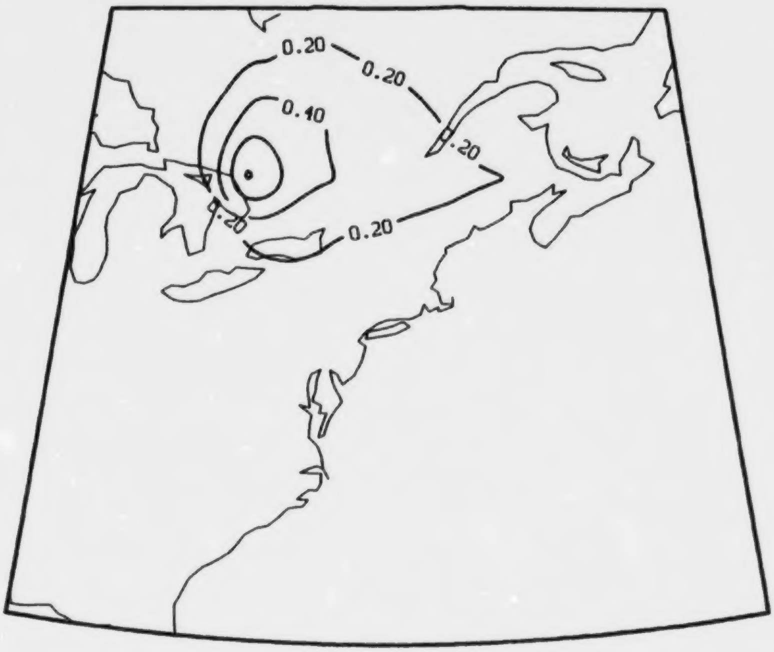
Figure 4 UW - LRT SIMULATION



SPATIAL DEPOSITION - FALL 1982. SUDBURY SOURCE

UW - LRT SIMULATION

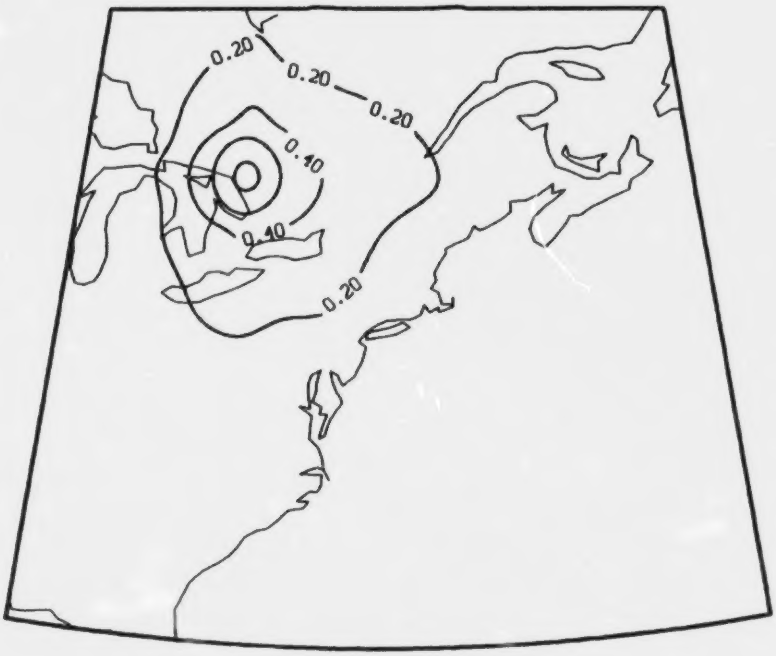
Figure 6



SPATIAL DEPOSITION - WINTER 1983. SUDBURY SOURCE

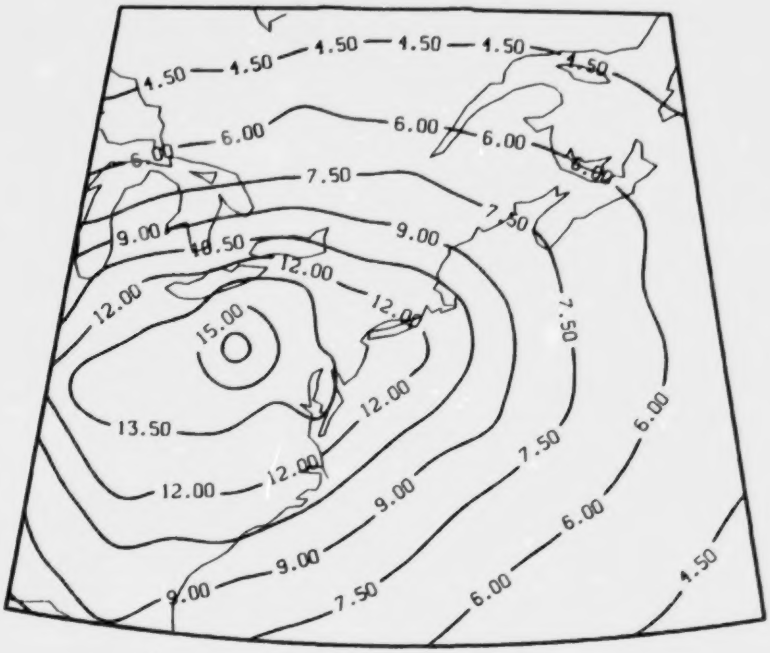
UW - LRT SIMULATION

Figure 5



SPATIAL DEPOSITION - SUMMER 1982. 73 SOURCES
(SUDBURY SOURCE OMITTED -- SMELTER SHUTDOWN)

Figure 7



SPATIAL DEPOSITION - FALL 1982. 73 SOURCES
(SUDBURY SOURCE OMITTED -- SMELTER SHUTDOWN)

Figure 8

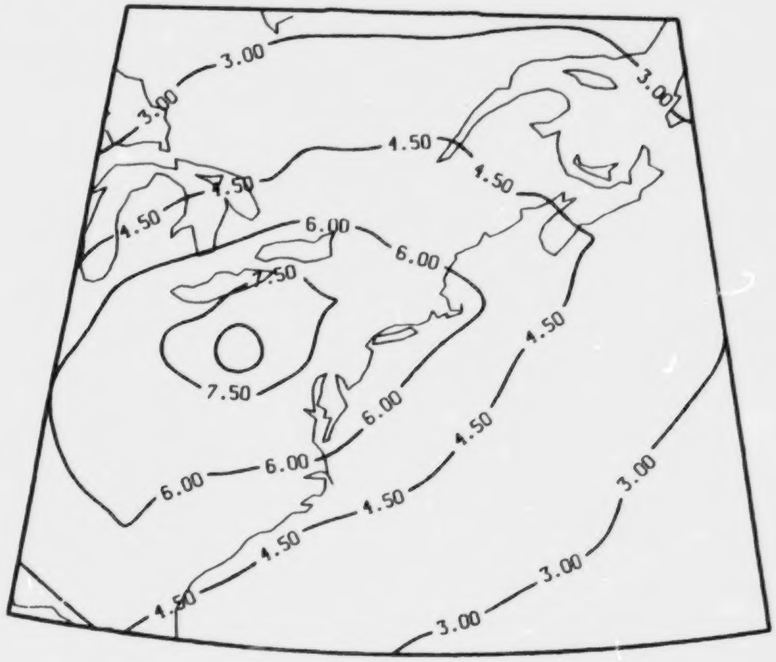


Figure 9 SPATIAL DEPOSITION - WINTER 1983. 73 SOURCES
(SUDBURY SOURCE OMITTED -- SMELTER SHUTDOWN)

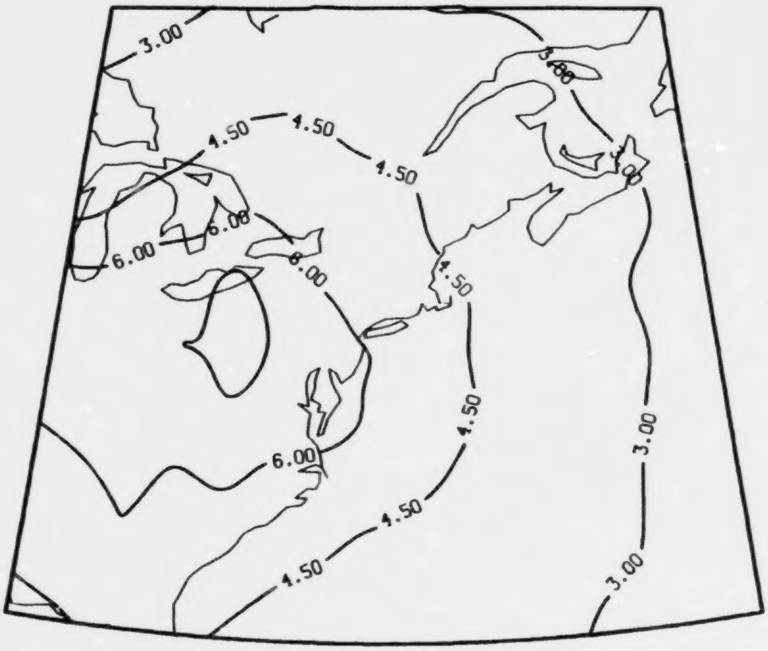
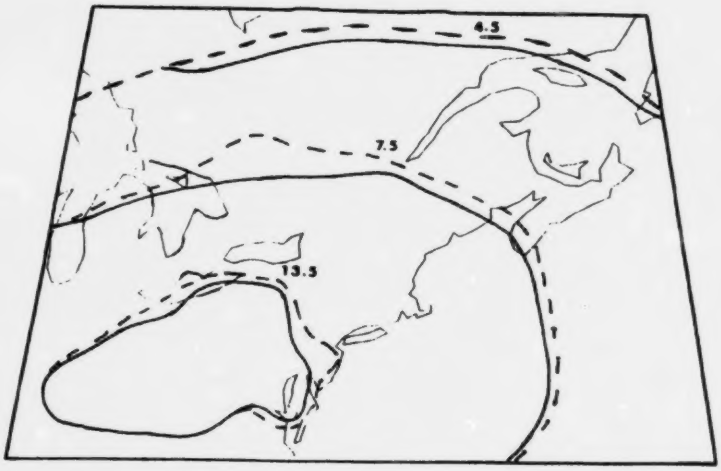


Figure 10
Composition of equivalent contours from figures 1 and 7.



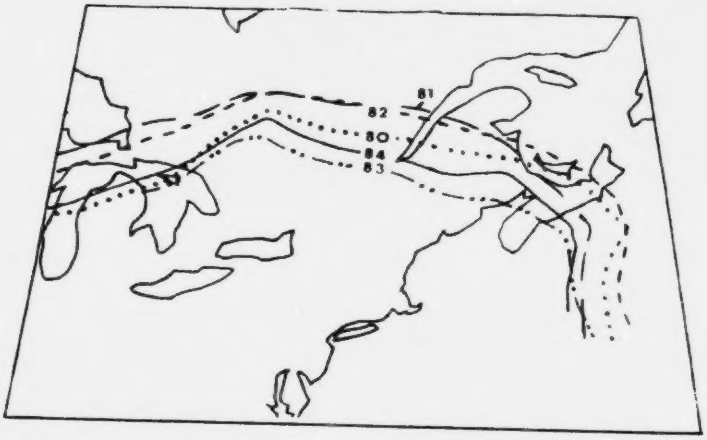


Figure 11
Locations of the 6.0 kg deposition contour for the summer season, 1980-84; UW-LRT Simulation.
(Units: kg SO_4/ha)

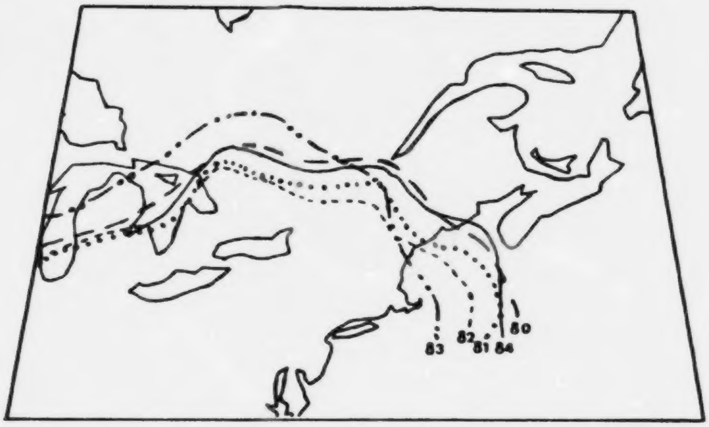


Figure 12
Locations of the 4.5 kg deposition contour for 1980-84, winter season; UW-LRT simulation.
(Units: kg SO_4/ha)

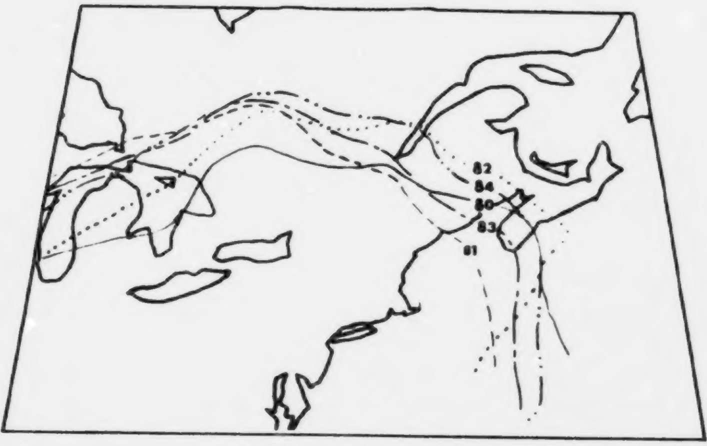


Figure 13
4.5 kg deposition contours for 1980-84, fall season; UW-LRT simulation
(Units: kg SO_4/ha)

Characterization of Building Wake Effects at Darlington Nuclear Generating Station using Sulfur Hexafluoxide (SF6) as a Tracer

G. Ogram* and H. Sahota

* Ontario Hydro Research Division
800 Kipling Ave.
Etobicoke

ABSTRACT :

The dispersion of materials released into the atmosphere from Darlington Nuclear Generating Station was studied using tracer gas techniques. Sulfur Hexafluoride was released from the vaccum building and the reactor building stack No.2. Tracer concentarions were measured dowinwind on an array of fixed samplers at the station boundary and by mobile monitor at various points between the release point and the site boundary. Simaltenoeus meteorological measurements were carried using acoustic sounders, anemometers and pibal-minisonde flights. Approximately forty hours of data were collected under different meterological conditions. Figure 1 shows the genral layout of the area and the sampling arcs.

Prliminary analysis of the data indicates that the plume centreline dilution factors at the site boundry are not strongly dependent on the atmospheric conditions, probably because the effects of building wake and complex terrain dominate. It was also observed that the tracer was entarined into the building wake on almost all occasions, leading to high ground level concentrations immediately downwind of the release. Site boundary dilution factors ranged from 8.2×10^{-7} s/m³ to 1.1×10^{-5}, a variation of only an order of magnitude.

INTRODUCTION :

Air flow aound buildings and other obstructions is quite complex and is chracterised by the presence of a wake region and one or more zones of recirculating secondary flows. Substantial literature exist on the theoratical and wind tunnel investigation of such flows. However there have been very few full scale experiments, primarily due to limitations in the istrumentations for characterizing the flow field and the logistics involved.

Dispersion of material emitted from the top a large structure is greatly influenced by the wake generated by the structure. Ontario Hydro operates two nuclear power generating stations located at Pickering Bruce and the third one at Darlington is under construction. Most of the emissions at these stations emanate from rooftop stacks and thus are affected by the building wake. In addition to the building wake effects all sites have reasonably complex topography. This paper describes a filed study which was carried out at Darlington to delineate the effects of building wake and topgraphy on dispersion of materials released from vaccum building and the reactor building.

Darlington Nuclear Generating Station is located on the northern shore of lake Ontario and is about 60 km east of Toronto. The main structure is about 600m (L) x 150m (W) x 50M (H). There is separate vaccum building which is circular and is also about 50m high. Topography around the buildings is quite complex. It rises sharply about 500 m from the building and goes up to about 60 to 70m height. On the west side there exists a large mound of excavated soil to the east there is undulating ground. The site boundary ranges from about 1 km to 2 km from the station depending on the direction.

EXPERIMENTAL METHODS :

Sulfur Hexafluoride (SF6), non toxic, colourles odourless gas was used as a tracer. The gas was released at a constant rate from a pressurized tank, using a regulator and a flow controller, through a 1/4 in. copper tube. Flow rate was typically 10 litres/min and was accurate to within one percent.

Concentraions of SF6 were measured using electron capture gas chromatography. The minimum detectable concentration was better than 5 pptv (parts per trillion by volume). At a concentration of 100 pptv, measurements were reproducible to within ten percent. Backflush arrangement was used to prevent oxygen from reaching the detector. This helped in keeping tha sample turnaround time to around two minutes.

Samplers were deployed along a fixed sampling arc, depending on the wind direction. The sampling arcs were matked at 100 m interval to facilitate in the deployment. Selected onsite roads were also marked at 50 or 100 m intervals to allow sampling of plume at shorter travel distances. Thirty sequential samplers constructed by the Research Division of Ontario Hydro were deployed along the site boundary so as to intercept the expected plume postion given the prevailing wind direction. Four sequential samples were taken with these samplers and one hour averaging time was always used.

In addition to the fixed samplers, a mobile SF6 sampleing system was setup by installing a GC in a avn. This enabled us to obtain instanteneous values of plume concentration. The mobile sampler was primarily used to define the plume profile near the release point to obtain information on the degree of plume entrainment and mixing due to the building wake. Some profiles were also taken along the site boundary for comaprison purposes.

A network of meteorological instruments was deployed to chracterise local atmospheric conditions during the experiments. The network consisted of two Bendix Frieze anemometers mounted at about 8.5 m, two monostatic acoustic sounders and a doppler acoustic sounder. In addition to onstie meteorological measuremnets, one acoustic sounder and a anemometer were installed about 6 km inland. Pilot balloon minisonde flights were also flown during most of the experiments. Data were recorded two additional on site tower whenever available. During the first phase of the experiment uvw anemometers were installed but dur to a storm they were damaged and only a limited data set were collected.

DISCUSSION OF RESULTS :

From Nov. 13, 1985 to June 16, 1986 eleven days were selected for the tracer release. A complete analysis of the data is underway and here we are presenting prelimanry results for Nov. 13, 18, and Dec. 2 1985.

Nov. 13, 1985:

On this day the winds did not turn onshore as anticipated so no data were collected on the asmpling arcs. Mobile sampling was carried out along the south access road that runs between the vaccum building and the lake. The plume was observed to be well mixed (Fig. 2). A maximum concentartion of 28.9 ppbv at ground level was seen at about 230 m from the release point. This coreesponds to a dilution factor of 3.5×10^{-4}. The plume also appears to consist of two components; a sharply peaked component of about 200 m measured width which corresponds to about 100 m plume width when corrected for of centre projection, and another much broader component of 2 to 3 times greater lateral dimension and of 10 to 100 times lower concentration. The fact that the two subsequent traverses gave closely matching profiles indicates that this dual mode structure is not an artifact of slowly changing wind direction , but may be due to the different effects of the vaccum and powerhouse building wakes.

Nov. 18, 1985 :

Mobile monitoring indicated a sharply defined plume within a few hundred meters of the powerhouse, clearly shown in the near lateral profile shown in Figs. 3 to 5. The latter profile was taken at about 200 m from the edge of the building and about 330 m from the release point. The winds were blowing almost parallel to the lenght of the building.

The apparent width of the plume (approximately 100 m) is close to the width of the building (about 140 m).

Dec. 2, 1985 :

Very high winds prevalied durind the entire sampling period. obile monitor data showed large fluctuations in concentartion with time at a fixed point. Fixed samplers on the EE arc showed a plume of about 200 to 250 m width and a centreline dilution factor between 8.9 x 10^{-7} and 1.7 x 10^{-6}. After release shutdown the concentration near the plume centreline on arc `c` appeared to decrease with a time constant of about 3 mins (Fig. 9).

DISCUSSION :

It was observed that the site boundary dilution factors (ratio of air concentration to the release rate) are not very senstive to the atmospheric conditions. In fact the dilution factors observed during the stable conditions are less than those observed under neutral or near neutral condtions. As expected, the tracer was inavariablly entrained in the building wake.The plume width always corresponded closely to the building dimensions. These are only preliminary findings. Further data analysis is underway to quantatively delineate the effects of building wake on the dispersion chracteristics of the Darlington Nuclear Generating complex.

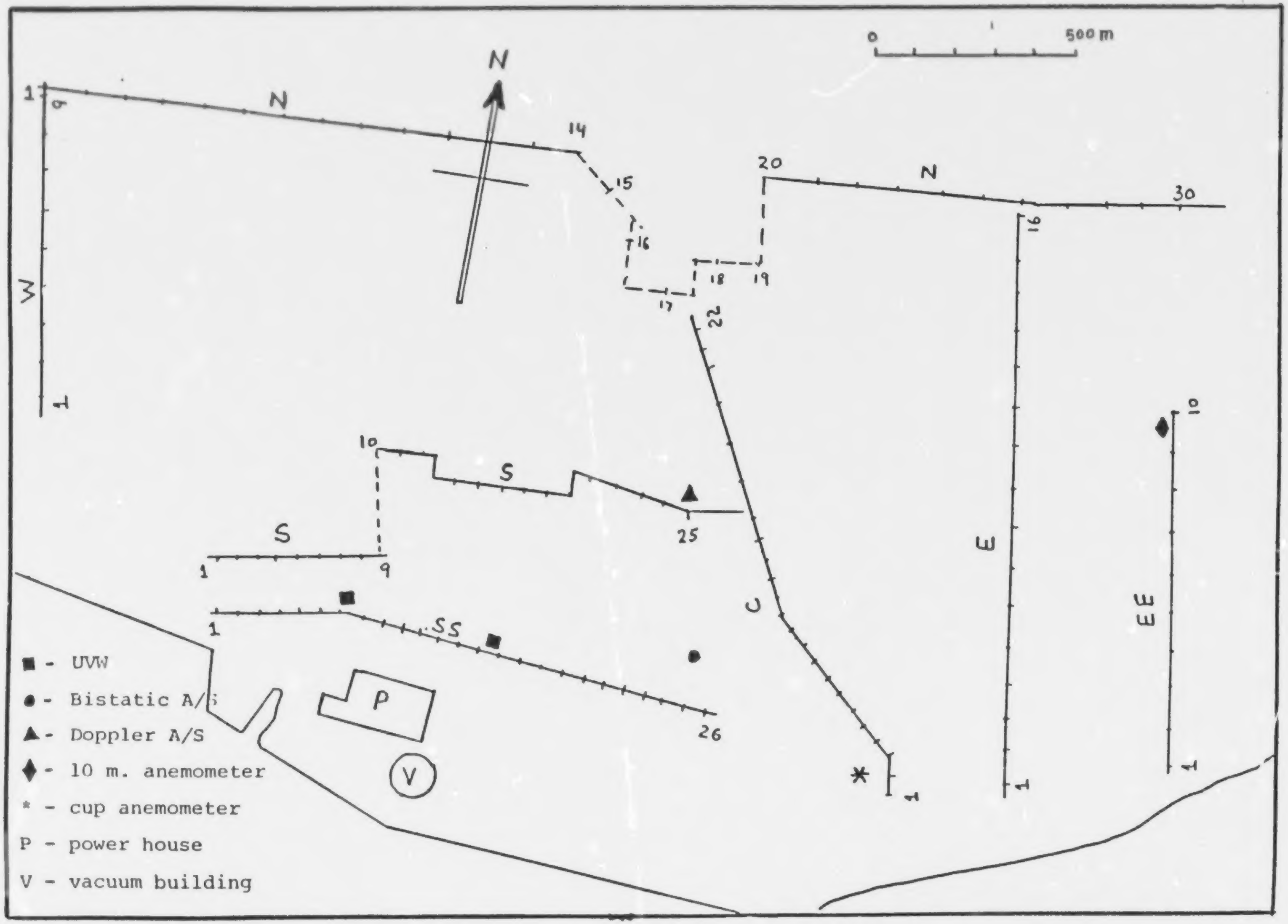


Fig.1 : Layout of Dailington Building Wake Experiment

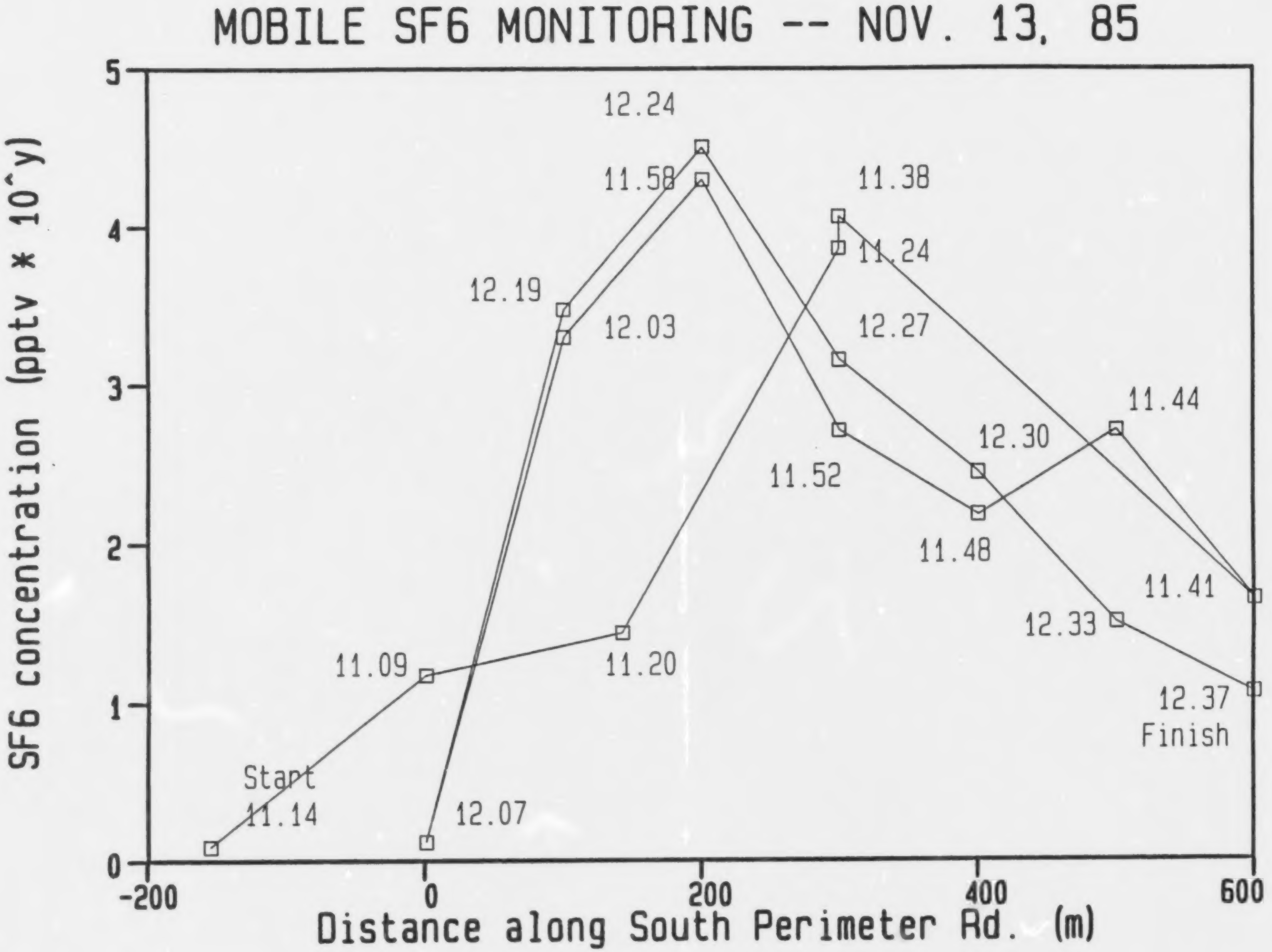

MOBILE SF6 MONITORING -- NOV. 13, 85
SF6 concentration (pptv * 10^y)
Distance along South Perimeter Rd. (m)
0
1
2
3
4
5
-200
0
200
400
600
Start
11.14
11.09
11.20
11.24
11.38
11.44
11.41
12.07
12.19
12.24
12.27
12.30
12.33
12.37
Finish
12.03
11.58
11.52
11.48

Fig. 2

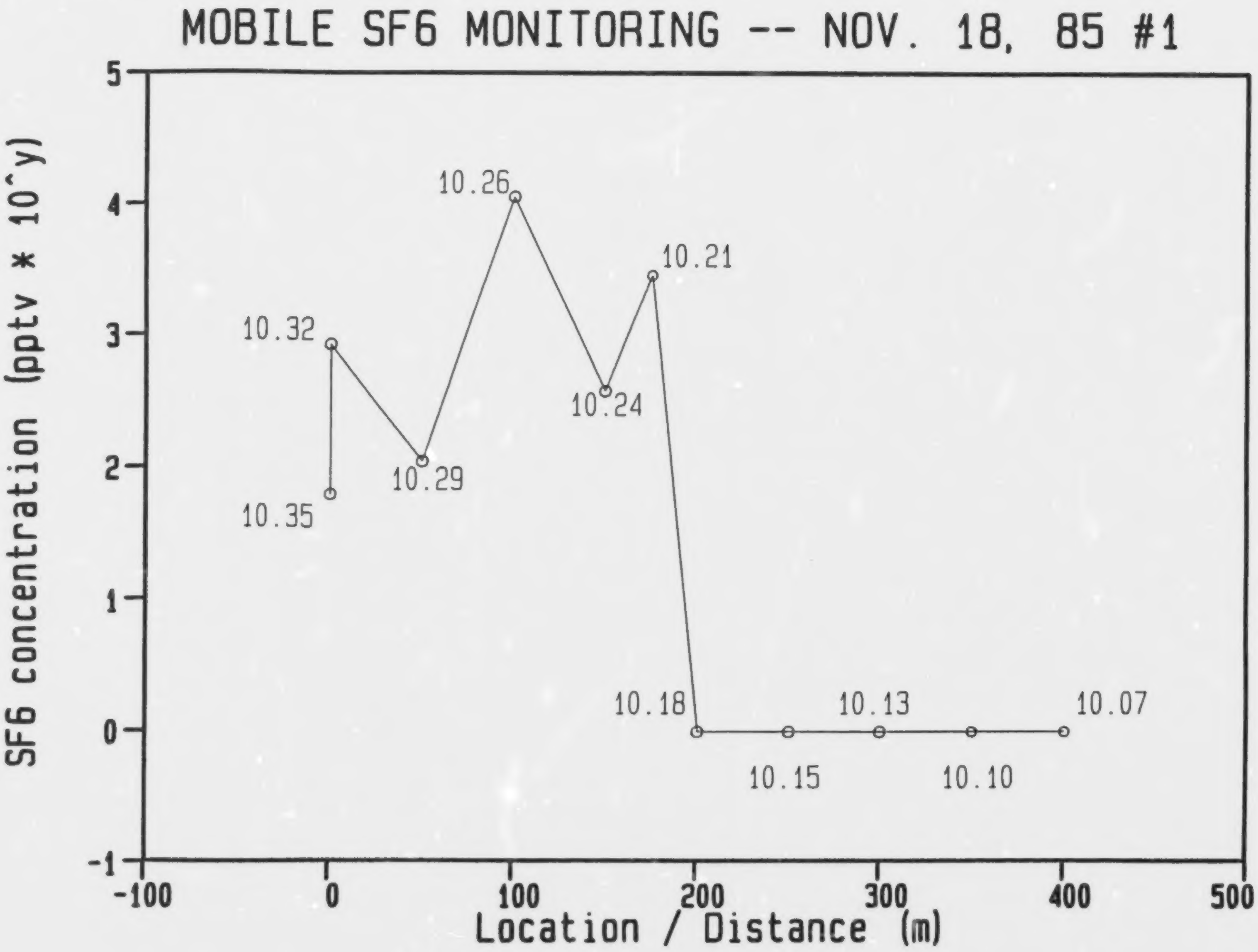


Fig. 3 : Sampling arc SS

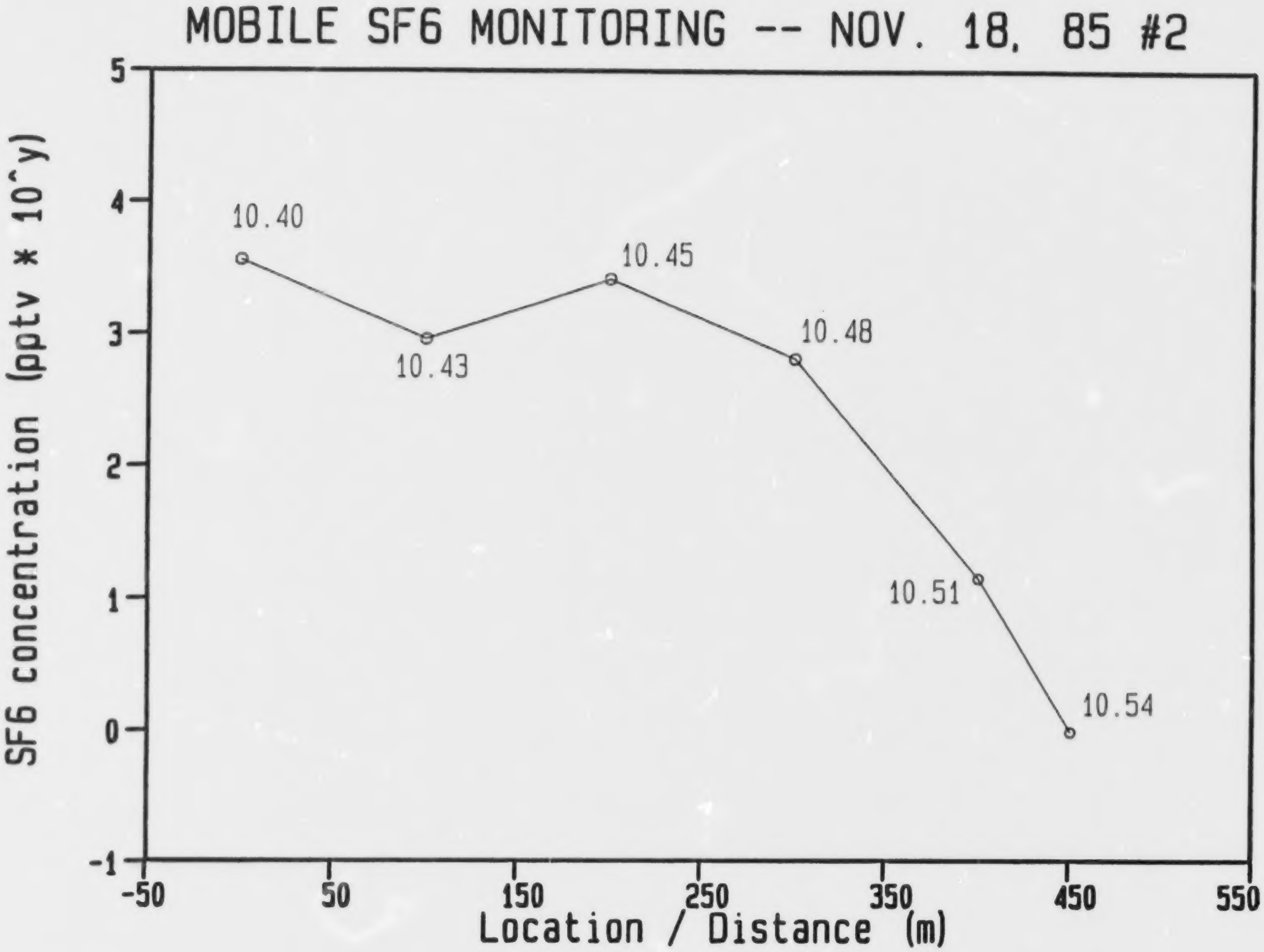


Fig. 4 : Sampling arc S

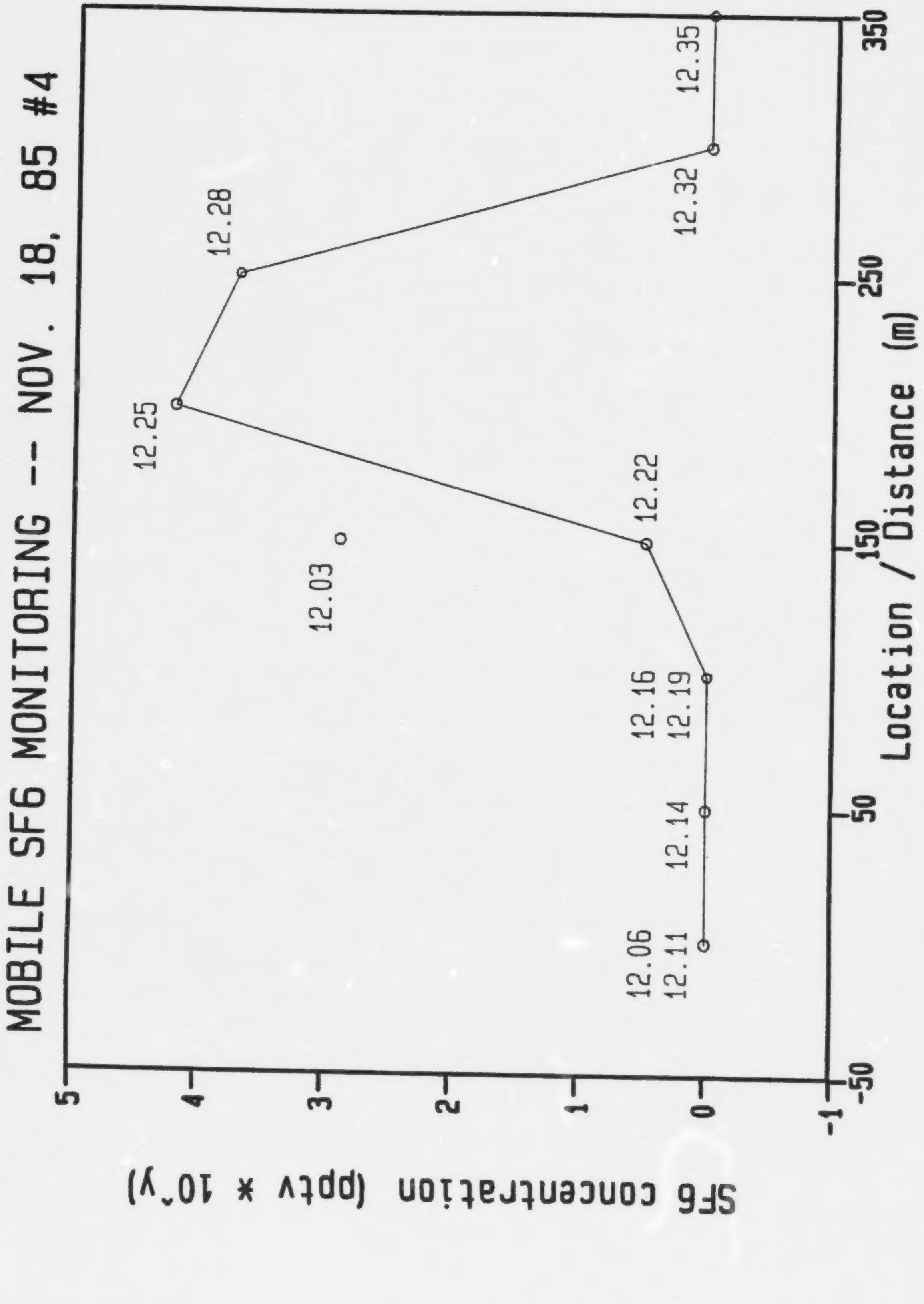


Fig. 5 : Sampling arc S. Fence

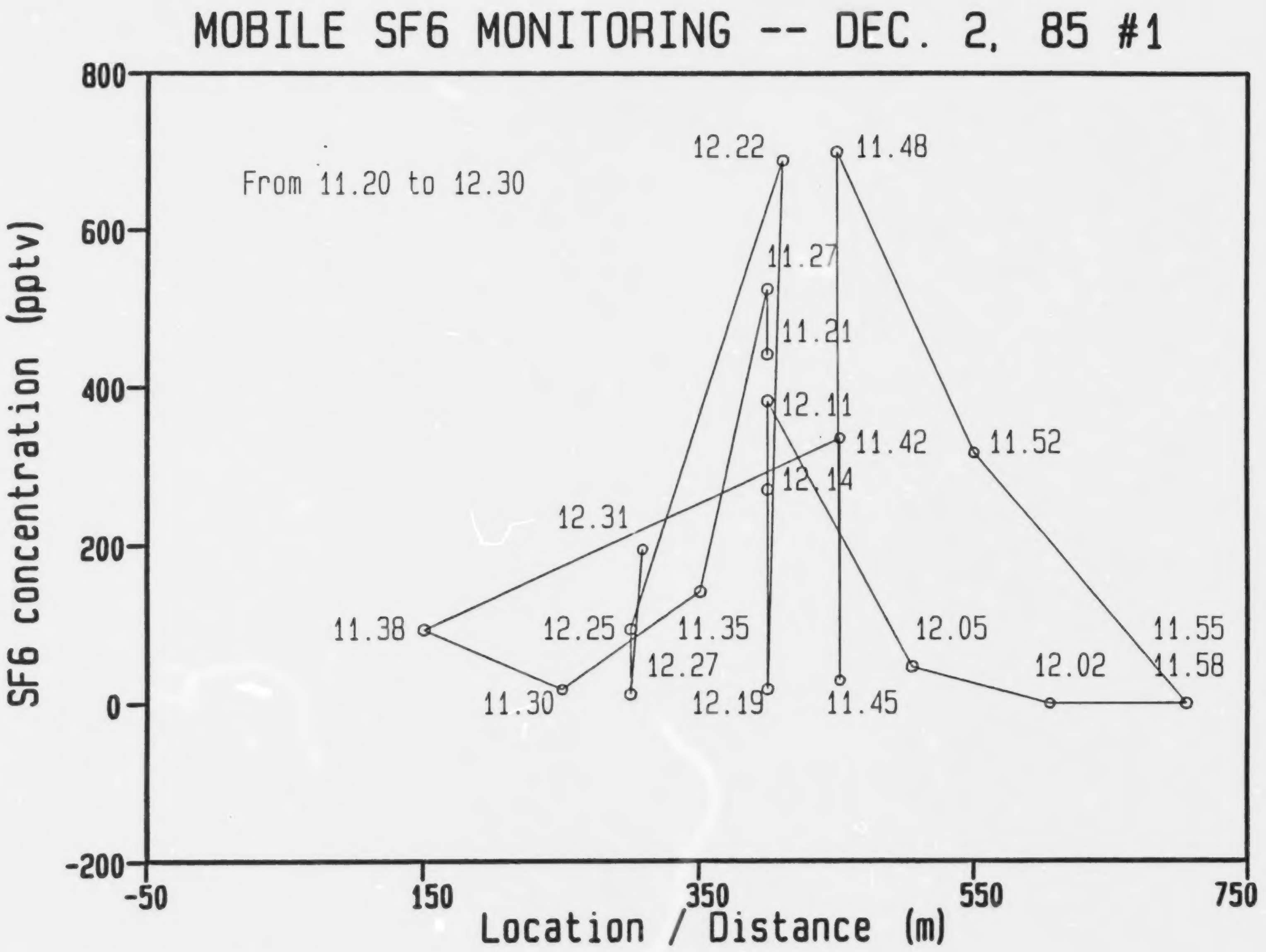


Fig. 6 : Sampling arc C

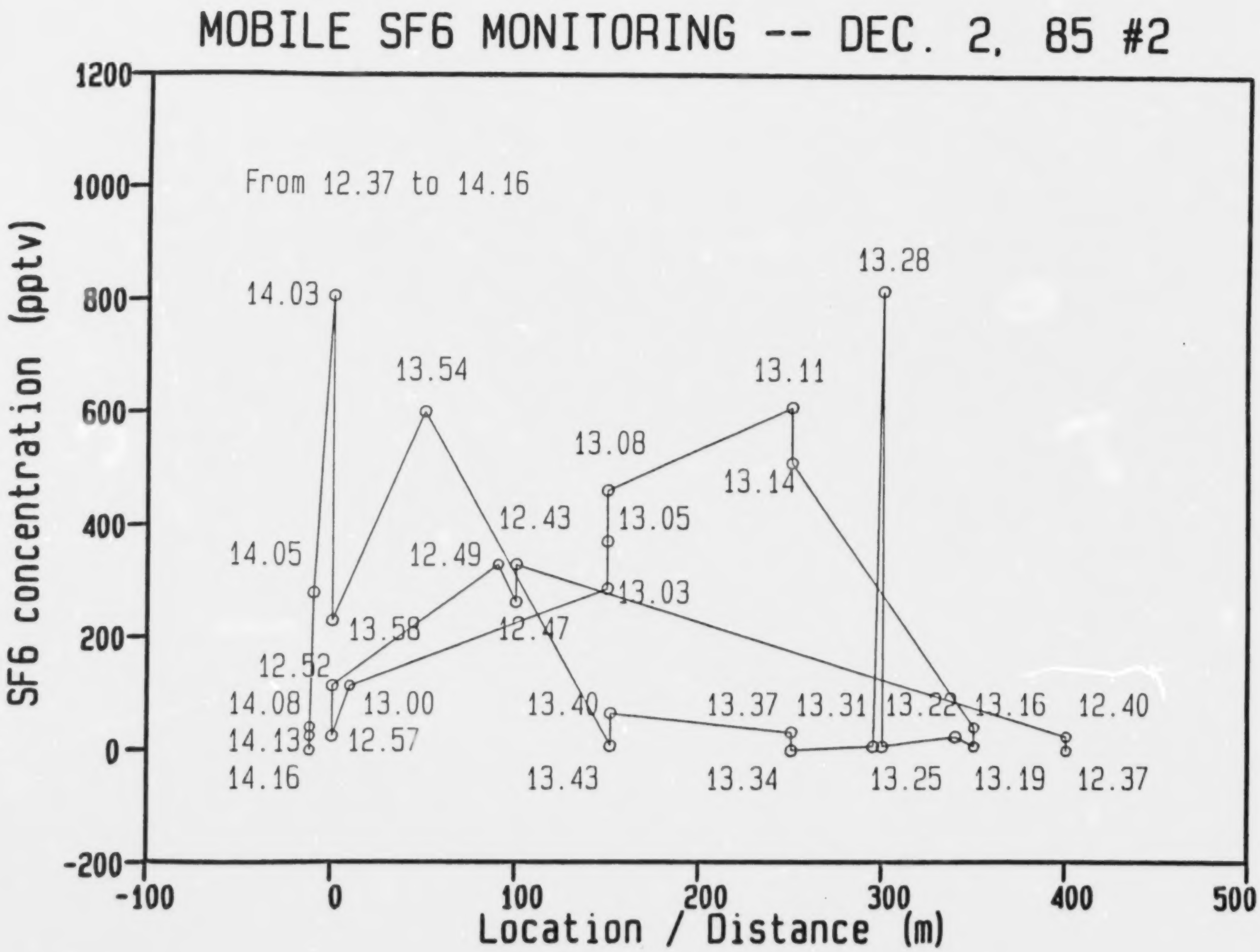


Fig. 7 : Sampling arc C

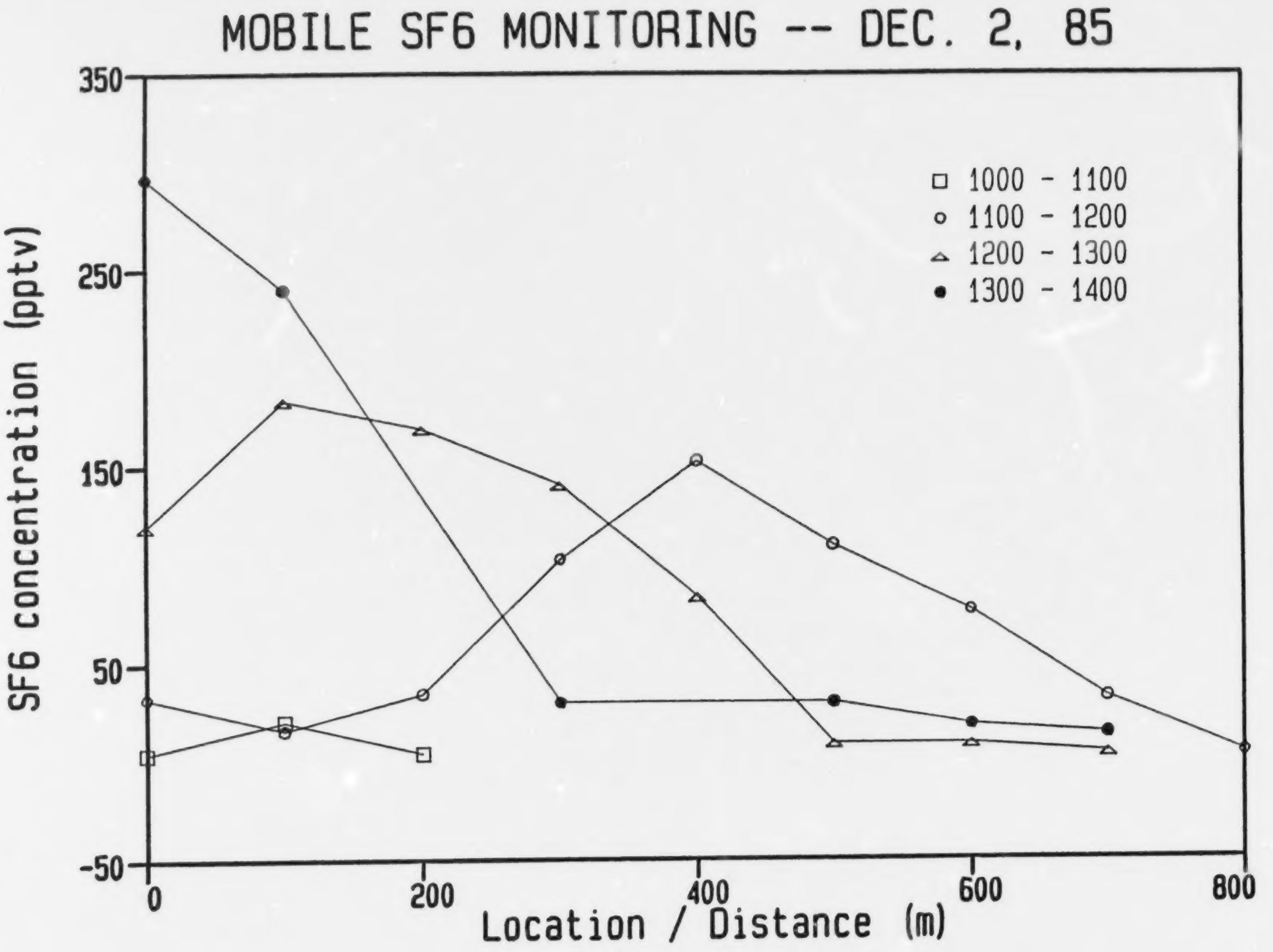


Fig. 8 : Sampling arc EE

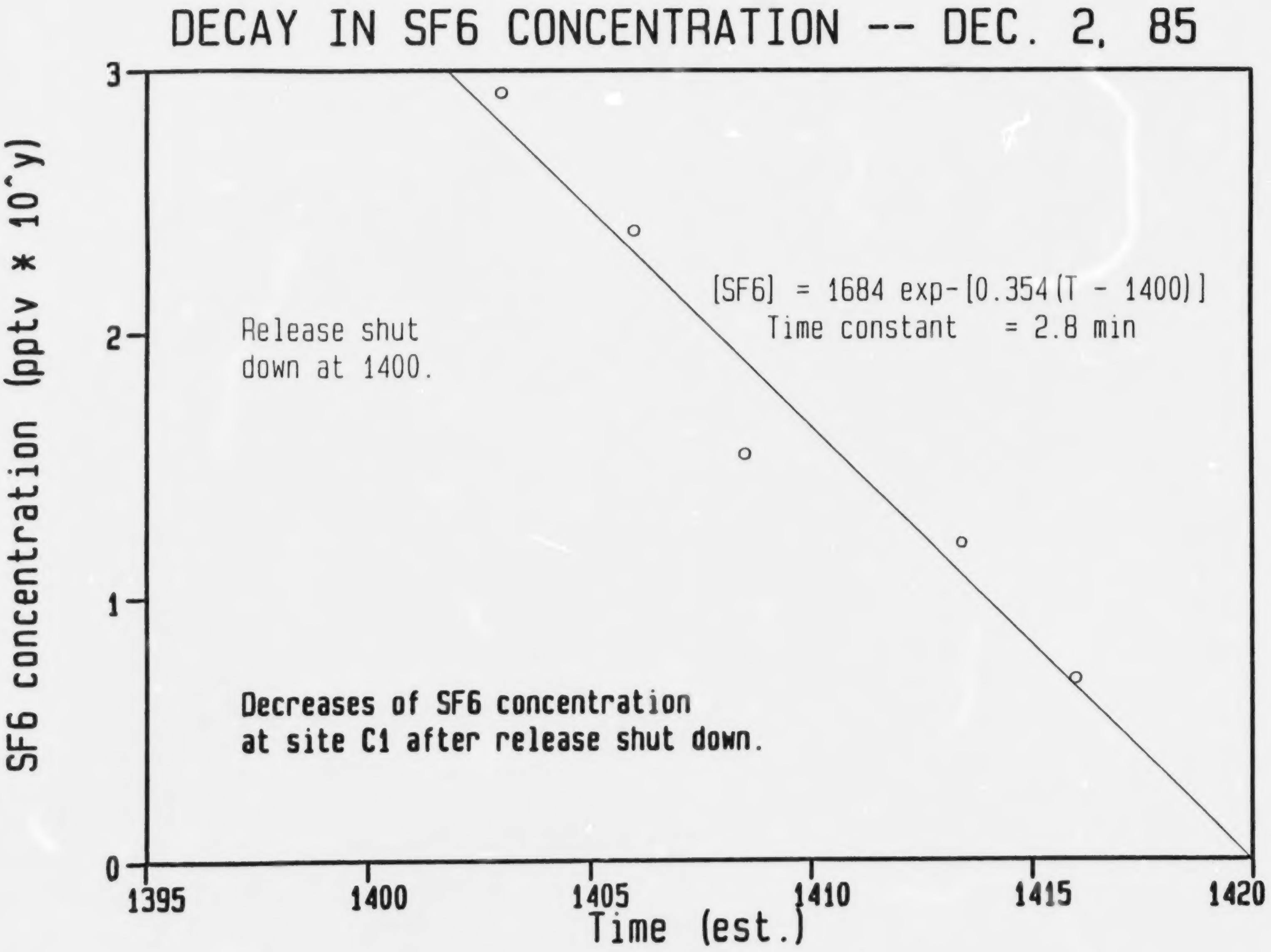

DECAY IN SF6 CONCENTRATION -- DEC. 2, 85
SF6 concentration (pptv * 10^y)
3
2
1
0
1395
1400
1405
1410
1415
1420
Time (est.)
Release shut
down at 1400.
[SF6] = 1684 exp-[0.354(T - 1400)]
Time constant = 2.8 min
Decreases of SF6 concentration
at site C1 after release shut down.

Fig. 9

TECHNOLOGY TRANSFER CONFERENCE 1986

Organized by RESEARCH ADVISORY COMMITTEE
J. Pagel, Chair

Sponsored by CORPORATE RESOURCES DIVISION
A. Castel, Executive Director

CONFERENCE COMMITTEE:

	M. Moselhy	***Co-ordinator***
Environment Ontario:	D. Bartkiw	G. Rees
	W. Chan	R. Reguly
	J. Donnan	G. Ronan
	D. McTavish	C. Schenk
	E. Piché	
Labour Ontario:	G. Wright	
Health Ontario:	L. Smith	
Environment Alberta:	H. Sims	
Environment Québec:	H. Saint-Martin	
Environment Canada:	F. Hurtubise	K. Shikaze
	B. Jank	
University of Waterloo:	J. Cherry	
Lakehead University:	G. Ozburn	
Goodfellow Consult. Inc.:	H. Goodfellow	
Zenon Environmental Inc.:	A. Benedek	
Communications:	T. Gorsline	C. Labonté
Poster Session:	H. Eijsenck	
Spouse Program:	Ann-Marie Clarke	

Volume

2

ISSN 0-825-4591

PROCEEDINGS

TECHNOLOGY TRANSFER CONFERENCE

December 8 & 9, 1986

The Sheraton Centre

External Research Projects

PART B
WATER QUALITY RESEARCH

Organized by
Research Advisory Committee

Sponsored by

Corporate Resources Division
Ministry of the Environment
Ontario
CANADA

Goal Statement

"To achieve and maintain a quality of the environment - including air, water and land - that will protect human health and the ecosystem and will contribute to the well-being of the people of Ontario."

ACKNOWLEDGEMENTS

The Conference Committee would like to thank the speakers and organizers for their valuable contributions.

DISCLAIMER

The views and ideas expressed in these papers are those of the authors and do not necessarily reflect the views and policies of the Ministry of the Environment, nor does mention of trade names or commercial products constitute endorsement or recommendation for use.

INTRODUCTION

The Ontario Ministry of the Environment holds its annual Technology Transfer Conference to report and publicize the progress made on Ministry-funded projects. These studies are carried out in Ontario universities and by private research organizations.

The papers presented at the Technology Transfer Conference held in December 1986 are presented in Conference Proceedings. These Proceedings are divided into five parts corresponding to the conference sessions dealing with:

Part A: Air Quality Research ;
Part B: Water Quality Research;
Part C: Liquid & Solid Waste;
Part D: Analytical Methods; and
Part E: Environmental Economics.

This part is a collation of those papers presented at Session B of the Conference.

For further information on any of the projects, the reader is kindly referred to the Principal Investigators or to the Research Management Office at (416) 965-5788.

Paper No. Page No.

INTRODUCTION

PART A: AIR QUALITY RESEARCH:

FEATURE PAPERS

A AN OVERVIEW OF ALBERTA ENVIRONMENT'S DEPOSITION RESEARCH PROGRAM 1
H.P. Sims: Director, Alberta Environment's Research Management Division, Alberta, Canada.

B MULTIMEDIA ANALYSIS AND ASSESSMENT OF ENVIRONMENTAL TOXIC AND CARCINOGENIC SUBSTANCES ... 29
R. Harkov: Office of Science and Research, New Jersey Dept. of Environmental Protection, New Jersey, U.S.A.

SESSION PAPERS

1 THE RAPID SCREENING OF MUNICIPAL REFUSE INCINERATOR FLYASH AND STACK GAS FOR PCDD/PCDF USING A TRANSPORTABLE TANDEM MASS SPECTROMETER (GC/MS/MS) SYSTEM 45
B. Shushan[1], A. Ngo[1], V. Ozvacic[2], G. Wong[2], G. DeBrou[2], B. Bobbie[2], R. Clement[2], S. Thorndyke[3] and B. Chittum[4]. 1-SCIEX, 2-Environment Ontario, 3-ORF, 4-Willington Consultants.

2 RETROSPECTIVE CORRELATION SPECTROSCOPY AND ITS APPLICATION TO ATMOSPHERIC MONITORING 59
R.W. Nicholls, M. Amani, M. Mandelman and W. Morrow, York University, Toronto, Ontario.

3 MEASUREMENT OF ATMOSPHERIC CONSTITUENTS BY TUNABLE DIODE LASER ABSORPTION SPECTROMETRY 64
H.I. Schiff, York University, Toronto, Ontario.

4 UPTAKE, DISTRIBUTION AND CLEARANCE OF SOLUBLE AEROSOLS IN THE HUMAN RESPIRATORY SYSTEM 81
W.J. Megaw[1] and J.F. Hicks[2]. 1-York University, Toronto, and 2-Environment Ontario.

5 EXPERIMENTALLY DETERMINED MUTATION RATES IN LUNG AS AN AIR QUALITY STANDARD 92
J. Heddle, A. Bouch, C. Couch, H. Kaul, J. Gingerich and K. Jain, York University, Toronto, Ontario.

Paper No. **Page No.**

6 **THE HAMILTON STUDY: EFFECTS OF FINE PARTICLES ON THE RESPIRATORY HEALTH OF SCHOOL CHILDREN** 106
L.D. Pengelly, A. Kerigan, C. Goldsmith, W. Furlong and S. Toplack, McMaster University, Hamilton, Ontario.

7 **BIOLOGICAL MONITORING OF ENVIRONMENTAL GENOTOXICITY** 134
M. Petras, J. Norsworthy, M. Vrzoc, and K. Hill, University of Windsor, Windsor, Ontario.

8 **FIELD AND LABORATORY VALIDATION OF A HIGH-VOL DENUDER FOR MINIMIZING PAH OXIDANT REACTIONS** 177
C.S. Davies[1], S. Guerin[1], J. Marr[2] and M. Quilliam[2]. 1-Concord Scientific Corp., 2-McMaster University, Ontario.

9 **A PARTICLE-SIZE SPECIFIC ELEMENTAL MASS BALANCE FOR APPORTIONMENT OF AMBIENT AEROSOL SAMPLED WITH MULTISTAGE FRACTIONATORS** 196
R.E. Jervis and T. Pringle, University of Toronto, Toronto, Ontario.

45 **MUTAGENICITY OF COMPLEX MIXTURES OF PAHS' IN AMBIENT AIR PARTICULATE MATTER** 206
A.S. Raj and M. Katz, York University, Toronto, Ontario.

46 **DOSE - RESPONSE STUDIES OF GASEOUS POLLUTANTS OF FOOD CROPS** 219
D.P. Ormrod and J. Petite, University of Guelph, Guelph, Ontario.

47 **PRODUCTION OF OZONE INSENSITIVE WHITE BEAN VARIETIES** 242
T.E. Michaels, University of Guelph, Guelph, Ontario.

48 **NICKEL CARBONYL AMBIENT MONITOR** 249
D.R. Hastie and H.I. Schiff, York University, Toronto, Ontario.

49 **ELEMENTAL COMPOSITION OF AIR PARTICULATES INSIDE AND OUTSIDE A BUILDING** 263
P. Harvey, J.D. McArthur and G. Palmer, Queen's University, Toronto, Ontario.

Paper No. Page No.

50 **STUDY OF THE THERMAL REACTIONS OF PCDD ON FLYASH PARTICLES UNDER INCINERATOR CONDITIONS** 277
L.C. Dickson and F.W. Karasek, University of Waterloo, Waterloo, Ontario.

51 **CONTINUOUS EMISSION MONITORING FOR TOTAL HYDROCARBON AT SEWAGE SLUDGE INCINERATORS** 305
J. Kosch, AMKO Systems Inc., Thornhill, Ontario.

52 **STUDY OF THE SPATIAL DISTRIBUTION OF THE IMPACT OF SUDBURY SMELTING EMISSIONS** 314
E.A. McBean, J. Byrne, J. Donald and G. Farquhar, University of Waterloo, Waterloo, Ontario.

53 **CHARACTERIZATION OF BUILDING WAKE EFFECTS AT DARLINGTON NUCLEAR GENERATING STATION USING SULPHUR HEXAFLUORIDE AS A TRACER** 330
G. Ogram[1], H. Sahota[2] and P.K. Misra[2].
1-Ontario Hydro, 2-Environment Ontario.

PART B: WATER QUALITY RESEARCH

FEATURE PAPERS

A **PREDICTIVE MODELS IN HAZARD ASSESSMENT OF GREAT LAKES CONTAMINANTS OF FISH** 1
Dora R. May Passino: U.S. Fish and Wildlife Service, National Fisheries Centre - Great Lakes, Ann Arbor, Michigan, U.S.A.

B **CONTROL OF TOXIC TRACE CONTAMINANTS IN MUNICIPAL WASTE WATER TREATMENT PLANTS** 27
Henryk Melcer: Biological Processes Section, Wastewater Technology Centre, Canada Centre for Inland Waters, Environment Canada, Burlington, Ontario, Canada.

SESSION PAPERS

10 **TRACE ORGANIC CONTAMINANT REMOVAL FROM DRINKING WATER** 52
J. Hilton, MacLaren Plansearch Inc., Toronto, Ontario.

11 **THE ROLE OF ORGANIC CARBON IN CONTROLLING THE OCCURRENCE OF DENITRIFICATION IN GROUNDWATER** 67
R.C. Starr and R.W. Gillham, University of Waterloo, Waterloo, Ontario.

Paper No.		Page No.
12	**REPRODUCTIVE OUTCOMES IN SOUTHWESTERN ONTARIO, 1980 TO 1985** .... J. McD. Robertson, H. Chan and I. Fyfe, University of Western Ontario, London, Ontario.	82
13	**ORGANIC CONTAMINANT STRUCTURE - PROPERTY - TOXICITY RELATIONSHIPS FOR AQUATIC ORGANISMS** ...... S. Abernethy and D. Mackay, University of Toronto, Toronto, Ontario.	113
14	**EFFECT OF LEAD, CADMIUM AND MERCURY ON THE TISSUE OF YOUNG FISH AND RATS: DEVELOPMENT OF BIOINDICATOR** .... D.M. Nicholls, R. Angelow, K. Tiechert-Kuliszewska and G. Girgis, York Univesity, Toronto, Ontario.	138
15	**IN-SITU ASSESSMENT OF MIXED COPPER AND ZINC IMPACTS ON WHITE SUCKER (Castastomus Commersoni) POPULATIONS IN SEVERAL NORTHERN ONTARIO LAKES: AN EVALUATION OF THE ENVIRONMENTAL HEALTH APPROACH TO VALIDATING WATER QUALITY CRITERIA** ..... K.R. Munkittrick and D.G. Dixon, University of Waterloo, Waterloo, Ontario.	165
16	**THE FATE OF TOXIC ORGANIC CHEMICALS IN SEWAGE TREATMENT PLANTS** .... B. Clark, S. Salenicks, J. Glynn Henry and D. MacKay, University of Toronto, Toronto, Ontario.	176
17	**TOXICITY OF PENTACHLOROPHENOL TO ZOOPLANKTON** ...... N.K. Kaushik and G. Stephenson, University of Guelph, Guelph, Ontario.	192
18	**DEVELOPMENT OF A STANDARD CLAM BIOMONITORING METHODOLOGY FOR THE DETECTION OF TRACE CONTAMINANTS WITHIN WATERS OF THE ONTARIO GREAT LAKES REGION** .... A. Melkic, E. Greece and D. Lewis, Integrated Explorations Ltd., Guelph, Ontario.	205
54	**EVALUATION OF DATA ON THE EFFECTS OF HYDRAULIC CHARACTERISTICS AND EFFLUENT CHLORINATION ON THE INCIDENCE OF MICRO-ORGANISMS OF PUBLIC HEALTH SIGNIFICANCE IN RECEIVING WATERS** .... M. Palmer, Gore & Storrie Ltd., Toronto, Ontario.	219
55	**LISTOWEL ARTIFICIAL MARSH TREATMENT PROJECT** .... J. Herskowitz, S. Black and W. Lewandowski, Ministry of the Environment, Toronto, Ontario.	244
56	**A LOW PRESSURE HYDROCYCLONE FOR USE IN SEWAGE TREATMENT** .... J.D. Boadway, Queen's University, Kingston, Ontario.	267

Paper No. **Page No.**

57 **THE EFFECTS OF RURAL AND SUBURBAN DEVELOPMENT ON SURFACE WATER QUALITY IN FIVE SELECTED SUBWATERSHEDS ON THE UPPER HUMBER RIVER** 294
B. Hindley, R. Hubbard and S. Maude, Metro Toronto Conservation Authority, Toronto, Ontario.

58 **HUMBER RIVER/BLACK CREEK: DETAILED BACTERIOLOGICAL WATER QUALITY STUDY EXAMINING THEIR IMPACT OF SEDIMENT AND SURVIVAL TIMES** 347
P.L. Seyfried and E. Harris, University of Toronto, Toronto, Ontario.

59 **FEASIBILITY OF PLANT HARVESTING IN WATER QUALITY AMELIORATION AND PHOSPHORUS MANAGEMENT IN SHALLOW IMPOUNDMENT** 392
P. McKee, K. Clarke-Whistler and G. Gaspardy, Beak Consultants Ltd., Toronto, Ontario.

60 **TWO BIOASSAYS FOR THE RAPID DETERMINATION OF THE EFFECTS OF DREDGED SEDIMENT DISPOSAL IN PRIMARY PRODUCTION AND PHOSPHORUS KINETICS IN OPEN WATERS** 415
C. Ewing and C. Nalewajko, University of Toronto, Scarborough, Ontario.

61 **STOCHASTIC ESTIMATION OF AMBIENT WATER QUALITY IN THE THAMES RIVER** 438
V.A. Graham, T.E. Unny and L. Logan, University of Waterloo, Waterloo, Ontario.

62 **OTTAWA RIVER NUCLEAR SPILL CONTINGENCY MODEL DEVELOPMENT: PHASE II** 467
T. Gowda, M. Palmer, C. Arnoldi and R. Jarvis, Gore & Storrie Ltd., Toronto, Ontario.

PART C: LIQUID & SOLID WASTE RESEARCH

FEATURE PAPERS

A **HAZARDOUS WASTE DESTRUCTION: AN OVERVIEW OF APPROACHES AND SHORTCOMINGS** 1
E. Timothy Oppelt: Thermal-Destruction Branch, Alternative Technologies Division, U.S.-EPA, Cincinnati, Ohio, U.S.A.

B **AN OUTLINE OF U.S.-EPA RESEARCH ON LAND DISPOSAL OF HAZARDOUS WASTE** 26
Norbert Schomaker: Hazardous Waste Engineering Research Lab., US-EPA, Cincinnati, Ohio, U.S.A.

Paper No. **Page No.**

SESSION PAPERS

19 **ASSESSMENT OF A PROTOTYPE SYSTEM FOR PYROLYSIS OF REFUSE DERIVED FUEL** 38
S.J. Thorndyke, Ontario Research Foundation, Mississauga, Ontario.

20 **MUNICIPAL SOLID WASTE FEASIBILITY OF GASIFICATION WITH PLASMA ARC** 63
G.W. Carter, Resorption Canada Ltd., Ottawa, Ontario.

21 **SEWAGE SLUDGE COMPOST AS TURF FERTILIZER** 78
J.L. Eggens, Ontario Agricultural College, University of Guelph, Guelph, Ontario.

22 **WASTE MANAGEMENT PLANNING FOR PHARMACEUTICAL INDUSTRY - PHASE I: INVENTORY AND DATA COLLECTION** 85
R. Makhija and R. Stairs, Tent University, Peterborough, Ontario.

23 **DEVELOPMENT OF GUIDELINES FOR THE UTILIZATION OF INDUSTRIAL WASTE IN BACKFILL AND CONSTRUCTION APPLICATIONS** 94
G. Zukovs, Canviro Consultants Ltd., Toronto, Ontario.

24 **NUMERICAL AND LABORATORY MODELLING OF TWO-PHASE FLOW IN POROUS MEDIA: 1 - TWO-PHASE GASEOUS FLOW, 2 - TWO-PHASE LIQUID FLOW** 117
G. Farquhar, E. McBean, J. Byrne, W. Abbott and R. Kell, University of Waterloo, Waterloo, Ontario.

25 **DEVELOPMENT OF POLYSULFIDE TECHNOLOGY FOR TREATMENT OF CONCENTRATED SPENT CYANIDE LIQUORS** ... 144
J.J. Gaczarczyk, University of Toronto, Toronto,

26 **TREATMENT OF LANDFILL LEACHATE BY SPRAY IRRIGATION** 175
R. McBridge, A.M. Gordon, P. Groenvelt, T. Bates and K. King, University of Guelph, Guelph, Ontario.

27 **CO-DISPOSAL OF INDUSTRIAL AND MUNICIPAL WASTES: PART II** 192
D. Kirk and M. Lau, University of Toronto, Toronto, Ontario.

63 **HAZARDOUS ORGANIC CHEMICALS IN GROUNDWATER AT ONTARIO LANDFILLS.** 206
J.F. Baker and J. Cherry, University of Waterloo, Waterloo, Ontario.

Paper No. **Page No.**

64 **DISPERSION OF THE STOUFFVILLE CONTAMINANT PLUME** 229
I. Proulx, R.N. Farvolden and E. Frind, University of Waterloo, Waterloo, Ontario.

65 **DEVELOPMENT OF DESIGN CRITERIA FOR OPTIMAL RECOVERY OF LEACHATE UNDER SANITARY LANDFILLS** 243
L. Arnaud, E. Frind, R. Farvolden and R. Gillham, University of Waterloo, Waterloo, Ontario.

66 **AN INVESTIGATION INTO THE REDOX CONDITIONS OF A LANDFILL LEACHATE PLUME CONTAINING VOLATILE ORGANICS, GLOUCESTER, ONTARIO** 272
L. Elliott, J. Develin, F. Michaels and W. Gorman, Queen's University, Kingston, Ontario.

67 **EFFECTS OF INCREASING AMOUNTS OF NON-POLAR ORGANIC LIQUIDS IN DOMESTIC WASTE LEACHATE ON THE HYDRAULIC CONDUCTIVITY OF CLAY LINERS IN SOUTHWESTERN ONTARIO** 294
R.M. Quigley and F. Fernandez, University of Western Ontario, London, Ontario.

68 **ASSESSMENT OF CONTAMINANT MIGRATION FROM INDUSTRIAL SOURCES DISCHARGING TO THE WELLAND RIVER** 315
M. Dickman, P. Hayes and I. Brindle, Brock University, St. Catherines, Ontario.

69 **EVALUATION OF CONTAMINANT VELOCITY GROUNDWATER IN LOW PERMEABILITY FRACTURE SHALE** 338
E. Sudicky, R. Blackport and J. Cherry, University of Waterloo, Waterloo, Ontario.

70 **GEOMECHANICAL INVESTIGATION OF NEAR-SURFACE FRACTURES IN CLAY TILLS** 349
M. Dusseault and A.Vorauer, University of Waterloo, Waterloo, Ontario.

71 **ORIGINS OF ELEVATED CHLORIDE CONCENTRATIONS IN GROUNDWATER SYSTEMS** 376
P.E. Pilon and K.W.F. Howard, University of Toronto, Scarborough, Ontario.

PART D: ANALYTICAL METHODS

FEATURE PAPERS

A **TRENDS IN MULTI-ELEMENT ANALYSIS: THE ROLE OF ICP-MS IN ENVIRONMENTAL APPLICATIONS** 1
Barry French, Institute for Aerospace Studies, University of Toronto, Toronto, Ontario, Canada.

Paper No. **Page No.**

B **DETECTION OF HYDROXYLATED NITRO-POLYNUCLEAR AROMATIC HYDROCARBONS AND KETONES IN AN AMBIENT AIR PARTICULATE EXTRACT USING BIOASSAY-DIRECTED FRACTIONATION** 31
Marcia G. Nishioka and Corrine C. Howard, Analytical Chemistry Section, Battelle Columbus Division, Columbus, Ohio, and Joellen Lewtas, U.S. - EPA, North Carolina, U.S.A.

SESSION PAPERS

28 **DIRECT SOLID SAMPLE ANALYSIS WITH THE DIRECT SAMPLE INSERTION DEVICE, PROMISE AND PROBLEMS** 64
E. Salin and R.L. Sing, McGill University, Montreal, Quebec.

29 **SCREENING METHODS FOR AIR AND WATER SAMPLES: APPLICATION OF INDUCTIVELY COUPLED PLASMA MASS SPECTROMETRY (ICP/MS) TO ELEMENTAL ANALYSIS** 74
J. Van Loon and B.French, University of Toronto, Toronto, Ontario.

30 **DEVELOPMENT OF SELENIUM ANALYSIS METHODOLOGY AT NG/L LEVELS FOR SOFT WATERS SUBJECT TO ACIDIC PRECIPITATION** 97
L.M. Brown and J. Wehr, University of Western Ontario, London, Ontario.

31 **EVALUATION AND OPTIMIZATION OF A TOC ANALYZER USING UV - PERSULPHATE DIGESTION** 111
R.D. Evans, Trent University, Peterborough, Ontario.

32 **DEVELOPMENT OF AN ULTRASONIC NEBULIZER FOR STABLE AND REPRODUCTIVE PRODUCTION OF AEROSOLS FOR ATOMIC SPECTROMETRIC ANALYSIS** 112
J.C. Van Loon, University of Toronto, Toronto, Ontario.

33 **DEVELOPMENT OF RECOMBINANT DNA PROBES TO DETERMINE THE ORIGIN OF FECAL STREPTOCOCCI AT THE TORONTO AREA BEACHES** 133
W.C. Bradbury, M.A. Marko, L. Papageorgiou, D. Leight and D. Rego, University of Toronto, Toronto, Ontario.

34 **PLANT BIOASSAYS FOR THE DETECTION OF ENVIRONMENTAL MUTAGENS** 147
Wm. F. Grant, McGill University, Montréal, Quebéc.

35 **A BIOLOGICAL INDICATOR SYSTEM TO IDENTIFY GENOTOXICITY OF IN-PLACE POLLUTANTS** 167
D.R. Hart, J. Fichko, M. Brinkman and P. McKee, IEC Beak Consultants Ltd., Mississauga, Ontario.

Paper No. **Page No.**

36 **FRESHWATER CLAMS AS MONITORS OF VARIATION IN ENVIRONMENTAL ACIDITY AND TRACE METAL LEVELS** 189
R.H. Green, S. Hinch and R. Bailey, University of Western Ontario, London, Ontario.

72 **ANALYSIS OF DIOXINS AND FURANS IN FISH AND OTHER BIOTA** 215
F.W. Karasek, T. Thompson, D. Schelenberg and K. Naikwadi, University of Waterloo, Ontario.

73 **DEVELOPMENT OF COST-EFFECTIVE PROTOCOL FOR ROUTINE ANALYSIS FOR TRACE ORGANIC CONTAMINANTS IN MUNICIPAL WPCP RAW SEWAGE AND FINAL EFFLUENT** 234
C. Chan[1], J. Martin[1], P. Pond[1], G. Rees[2], and T. Ho[2]. 1-Mann Testing Labs. Ltd., 2-Environment Ontario.

74 **APPLICATION OF GC HELIUM MICROWAVE PLASMA DETECTION TO THE RAPID SCREENING OF CHEMICAL WASTE** 255
M. Danszinger, Barringer Magenta Ltd., Rexdale, Ontario.

75 **DEVELOPMENT OF METHODS SUITABLE FOR THE USE IN THE AMES SALMONELLA MUTAGENICITY ASSAY FOR THE COLLECTION OF ORGANICS PRESENT IN GROUNDWATER AND LANDFILL SITE MATRIX MAERIALS** 271
G.H. Thomas, A. Horton and K. Matsummura, Ontario Research Foundation, Mississauga, Ontario.

76 **SYNTHESIS OF OXYGEN AND SULPHUR PAHS OF INTEREST IN ENVIRONMENTAL POLLUTION** 294
E. Lee-Ruff and F. Ablenas, York University, Toronto, Ontario.

77 **DEVELOPMENT OF A ROBOTIC WORKSTATION FOR THE ROUTINE ANALYSIS OF ORGANICS IN BIOLOGICAL TISSUES USING ACID DIGESTION AND SOLVENT EXTRACTION METHOD** 298
C. Chan[1], J. Martin[1], G.Ladwig[1], G. Rees[2], and G. Crawford[2]. 1-Mann Testing Labs Ltd., 2-Environment Ontario.

78 **SEPARATION AND IDENTIFICATION OF ORGANIC COMPOUNDS IN EXTRACTS OF AIR PARTICULATES BY HPLC AND GC/MS** 331
K.P. Naikwadi, G. Charbonneau and F.W. Karasek, University of Waterloo, Waterloo, Ontario.

Paper No. **Page No.**

79 QUANTITATIVE DETERMINATION OF SELECTED PAHS' BY SHPOL'SKII AND JET-COOLED SPECTROSCOPY 355
C.M. Sadowski, J. Lai, H. Malle, S. Filseth and F. Morgan, York University, Toronto, Ontario.

80 NEW SYNTHETIC METHODOLOGY FOR THE EXPEDIENT PROVISION OF PURE PAH ANALYTICAL STANDARDS 384
V.A. Snieckus, University of Waterloo, Waterloo, Ontario.

PART E: ENVIRONMENTAL ECONOMICS

FEATURE PAPER

A THE ENVIRONMENT OF ECONOMICS - PAST PRESENT AND FUTURE ROLES OF ECONOMICS IN ENVIRONMENTAL MANAGEMENT 1
Clifford Russell, Director, Institute for Public Policy Studies, Vanderbilt University, Nashville, Tennesee, U.S.A.

SESSION PAPERS

37 ABATEMENT COST FUNCTIONS - THE WORKHORSE OF ENVIRONMENTAL MANAGEMENT 18
J. Donnan, C. Griffith, S. Glover and M. Dandele, Policy & Planning Branch, Ministry of the Environment, Toronto, Ontario.

38 MEASURING THE SOCIAL COSTS OF ELECTRICAL EXPORTS AND COST RECOVERY OPPORTUNITIES OF ENVIRONMENTAL PROTECTION OF ONTARIO HYDRO 39
W. Wianko and B. Green, Ontario Hydro, Toronto, Ontario.

39 QUÉBEC'S EXPERIENCE WITH THE ECONOMIC EVALUATION OF ENVIRONMENTAL REGULATIONS - WHAT LESSONS HAVE BEEN LEARNED 65
C. Sauvé, Ministére de l'Environment, Sainte-Foy, Québec.

40 3M'S POLLUTION PREVENTION PAYS PROGRAM 77
A.G. Mills, 3M Canada Inc., London, Ontario.

41 THE BENEFITS OF REDUCING LEAD IN U.S. DRINKING WATER 87
R. Levin, U.S.-EPA, Washington, D.C., U.S.A.

Paper No.		Page No.
42	**ECONOMIC EFFECTS OF REDUCED FOREST GROWTH IN THE UNITED STATES' FOREST ECONOMY AND ON CANADIAN-U.S. LUMBER TRADE** .... J.M. Callaway, Jr., Battelle Northwest Labs, Richland, Washington, U.S.A.	112
43	**SOME ECONOMICS OF THE GRAND CANAL** .... A. Muller, Department of Economics, McMaster University, Hamilton, Ontario.	129

Predictive Models in Hazard Assessment of Great Lakes Contaminants for Fish[1]

Dora R. May Passino

U. S. Fish and Wildlife Service

National Fisheries Center-Great Lakes

Ann Arbor, Michigan 48105

U.S.A

Key words: Structure-Activity Relationships, QSAR, *Daphnia*, Acute Toxicity, Linear Solvation Energy Relationships.

ABSTRACT

A hazard assessment scheme was developed and applied to predict potential harm to aquatic biota of nearly 500 organic compounds detected by gas chromatography/mass spectrometry (GC/MS) in Great Lakes fish. The frequency of occurrence and estimated concentrations of compounds found in lake trout (*Salvelinus namaycush*) and walleyes (*Stizostedion vitreum vitreum*) were compared with available manufacturing and discharge information. Bioconcentration potential of the compounds was estimated from available data

---

[1] Contribution 670, National Fisheries Center-Great Lakes, Ann Arbor, Michigan 48105, U.S.A.

or from calculations of quantitative structure-activity relationships (QSAR). Investigators at the National Fisheries Center-Great Lakes also measured the acute toxicity (48-h EC50's) of 35 representative compounds to Daphnia pulex and compared the results with acute toxicity values generated by QSAR. The QSAR-derived toxicities for several chemicals underestimated the actual acute toxicity by one or more orders of magnitude. A multiple regression of log EC50 on log water solubility and molecular volume proved to be a useful predictive model. Additional models providing insight into toxicity incorporate solvatochromic parameters that measure dipolarity/polarizability, hydrogen bond acceptor basicity, and hydrogen bond donor acidity of the solute (toxicant).

INTRODUCTION

Natural resource and regulatory agencies are confronted with evaluating a vast and growing number of chemicals that have been detected in the aquatic environment or will be potentially released into it. At the same time, the abundance and diversity of aquatic species has diminished in many areas. In the Great Lakes, chemical contaminants have been suspected of playing a causal role in such fishery resource problems as the increase in the incidence of cancerous tumors in brown bullheads, Ictalurus nebulosus (Baumann 1984), and the reproductive impairment of lake trout, Salvelinus namaycush (Mac et al. 1985). A hazard assessment of the chemicals in the environment and the biota is the first step in evaluating the role of chemicals in fishery resource problems.

As a result of monitoring efforts to detect known and previously unrecognized contaminants in fish from the open waters of the Great Lakes, 476 organic chemicals were tentatively identified in lake trout and walleyes, Stizostedion vitreum vitreum, from the Great Lakes and Lake St. Clair (Hesselberg and Seelye 1982). Detection of such a large array of compounds in fish raises several questions about the sources of the compounds and their potential impacts on fish and other biota, and ultimately about the need for regulatory control of the compounds. Consequently, this long list of chemicals served as a starting point for an assessment of the hazard of various classes of organic chemicals to the aquatic biota in the Great Lakes (Passino et al. 1986; National Fisheries Center-Great Lakes 1986).

At an early stage in the hazard assessment, I discovered that not only were there no consistent data sets for aquatic toxicity or other factors important for assessment of most of these chemicals, but there were no biological data for many of them. Hence, my colleagues and I at the National Fisheries Center-Great Lakes conducted a series of acute bioassays with Daphnia pulex under constant conditions to generate a data set that could be used for comparing classes of chemicals. Even so, the number of data needed to evaluate this huge array of chemicals exceeded the practical capabilities of conducting bioassays. Consequently, other approaches to screening chemicals for hazard to aquatic organisms were clearly required.

A supplemental method for generating experimental data to evaluate chemicals is the use of quantitative structure-activity relationships (QSAR), whereby physical and chemical properties of compounds are used to estimate toxicity, bioaccumulation, and behavior of chemicals in the environment. The origin of this approach can be traced to Crum Brown and Fraser (1868-1869) who suggested that biological activity could depend on aqueous solubility and to Meyer (1899) and Overton (1901) who independently discovered that lipid solubilities of chemicals could predict the narcotic effect of chemicals on organisms. The extensive use of QSAR in modern drug design originated with the pioneering work of Corwin Hansch and his colleagues (Hansch and Fujita 1964; Hansch 1971), which led to the development of many basic models useful to toxicologists. More recently aquatic toxicologists and chemical regulatory agencies such as the U.S. Environmental Protection Agency (USEPA) have screened environmental chemicals with QSAR models (Kaiser 1984; Kamlet 1986); however, the data available to verify the models and their predicted values are notably sparse. The QSAR models for aquatic toxicology and hazard assessment are still in their early stages of development.

The QSAR models most often applied in aquatic toxicology depend on solubility of chemicals in water or their lipophilicity as usually measured by the partitioning (P) of the chemical between water and octanol (Dearden 1985). Several solubility terms, including molecular weight (MW) and molecular volume (MV), which affect the bioaccumulation of chemicals in aquatic organisms (Neely et al. 1974), can be related to toxicity either by simple linear regression or multiple linear regression. The generalized empirical equation of Hansch (Könemann 1981) included a square of the partitioning coefficient as well as terms relating to acid dissociation and steric parameters of the chemicals (solutes).

Kamlet et al. (1986a; 1986b) recently demonstrated that many "pharmacological and toxicological properties that depend on solute-solvent interactions can be correlated, rationalized and predicted in terms of a single generalized linear solvation energy relationship of simple and conceptually explicit form"(Kamlet el al. 1986b). Solubility and solvent-dependent properties, XYZ, including toxicological properties, are well correlated by equations that include linear combinations of free energy or enthalpy contributions of three types of terms (Kamlet et al. 1986c):

$$XYZ = XYZo + \text{cavity term} + \text{dipolar term} + \text{hydrogen bonding term(s)} \qquad (1)$$

"The cavity term is a measure of the free energy necessary to separate the solvent molecules (overcome solvent-solvent interactions) to provide a suitably sized cavity for the solute......The dipole term is a measure of the exoergic effects of solute-solvent, dipole-dipole, dipole-induced dipole, and dispersion interactions. The solute and solvent parameters that influence this term are π_1* and π_2* where π* is the solvatochromic parameter that is a measure of the ability of a compound to stabilize a neighboring charge or dipole by virtue of its dielectiric effect....The hydrogen bonding terms describe the exoergic effects of complexation between HBD (hydrogen bond donar) solvents and HBA (hydrogen bond acceptor solutes), denoted as α_1 and $(\beta m)_2$...; α and β are the solvatochromic parameters that characterize the HBD acidity and HBA basicity, i.e., they express the abilities to donate and accept a proton to form a hydrogen bond" (Kamlet et al. 1986c).

The generalized equation given by Kamlet et al. (1986a) may be simplified for the situation dealing with solubility properties of multiple solutes in single solvents (as in the present case); the simplified equation relates specifically to solute parameters:

$$SP = SPo + m^{V}I/100 + s\pi^* + a(\alpha_m) + b(\beta_m) \qquad (2)$$

Where $V_I/100$ = computer calculated intrinsic (van der Waals) molecular volume (Moriguchi et al. 1976)

π^* = dipolarity/polarizability term

α_m = hydrogen-bond donor acidity term

β_m = hydrogen-bond acceptor basicity term.

The term $V_I/100$ is used so that the parameter measuring the cavity term is of the same order of magnitude as the other independent variables, thus facilitating the comparison of the relative contributions of the terms.

The purposes of the present paper are to (1) present an approach to hazard assessment of chemicals detected in Great Lakes fish, (2) demonstrate the need for toxicity data sets for hazard assessment, and (3) demonstrate the use of several QSAR models to predict toxicity of several classes of chemicals to Daphnia pulex, a representative freshwater zooplankter from the Great Lakes.

MATERIALS AND METHODS

The 476 chemicals that served as the focal point of this hazard assessment were tentatively identified by gas chromatography/mass spectrometry using a Finnigan 4023 quadrapole GC/MS[2] with an Incos data system (Passino et al. 1986). After grouping the chemicals into about 50 classes, Passino et al. (1986) developed a provisional hazard ranking of the classes based on available data on aquatic toxicity bioconcentration, occurrence in fish, and potential sources. Because data were sparse for aquatic toxicity--the factor considered most important in evaluating hazard--the National Fisheries Center-Great Lakes (1986) conducted acute toxicity bioassays with Daphnia pulex, using 30 chemicals representative of the 19 classes that were highest in the provisional hazard ranking.

My colleagues and I calculated a revised hazard ranking of classes that incorporated acute toxicity data developed for D. pulex (National Fisheries Center-Great Lakes 1986), information on occurrence and abundance of the chemicals in Great Lakes fish (Hesselberg and Seelye 1982), and potential sources of the chemicals (Passino et al. 1986). Each chemical class was assigned a rank relative to the other classes for each category (toxicity, occurrence, and source). For each class and category a weighted ratio was calculated as follows:

---

[2] Use of trade names or manufacturer's names does not imply U.S. Government endorsement of commercial products.

$$\text{weighted ratio} = (\text{rank}/\text{maximum rank}) \times \text{weight} \qquad (3)$$

The weights were selected on the basis of estimated relative contribution of each category to the hazard of the chemicals and on the accuracy of the information for that category. The weighted ratios of each category for a given class were summed to determine a hazard ranking value for each class.

Acute bioassays were completed with D. pulex for 35 representative and related chemicals from the following top-ranked classes for which available toxicity data were deemed inadequate to evaluate the hazard of the classes (National Fisheries Center-Great Lakes 1986; Perry 1986): polyaromatic hydrocarbons (PAHs), alkyl halides, monocyclic and polycyclic alkanes, heterocyclic nitrogen compounds, other nitrogen-containing compounds, and silicon-containing compounds (alkylether silanes). The acute bioassays with D. pulex followed established methods of National Fisheries Center-Great Lakes (1986) and Passino and Novak (1984) with temperature at 20 C in reconstituted hard water.

Passino and Smith (1986) used the following parameters from a QSAR data base as independent variables for regressions of the natural logarithm of the measured acute toxicity (log EC50) to D. pulex: calculated acute toxicity to Daphnia (QSAR log LC50), logarithm of the octanol-water partitioning coefficient (log P), water solubility (Cw), and molecular volume (MV). The molecular volume was the molecular weight of the chemical divided by its liquid density. These QSAR estimates were obtained from the data base of USEPA, Duluth, Minnesota, which is accessible at Montana State University, Center for Data Systems and Analysis. The actions of chemicals on living systems are better understood in terms of the number of molecules present than in terms of the weight of the chemicals. Hence, Passino and Smith (1986) calculated regressions for concentrations expressed both as μM and mg/L. For the solvatochromic models, I obtained the values for $V_I/100$, π^*, α_m, and β_m from Kamlet (1986a; 1986b; 1986c; personal communication). Linear regression analysis, covariance analysis for class differences, quadratic equations, and multiple regressions were computed with SAS (SAS Institute Inc. 1985).

RESULTS AND DISCUSSION

I focused my attention on estimating the hazard of the highly ranked classes of chemicals and representative chemicals within the classes, rather than on individual chemicals because the identification of the 476 chemicals by GC/MS was only provisional. An initial attempt to confirm the identitiy of 10 of the 476 chemicals by comparison with standards indicated that the unknowns in the fish shared important structures in common with these standards, but that the unknowns were not identical to the standards (James P. Hickey, National Fisheries Center-Great Lakes, personal communication). Hence, I emphasized the structure-activity relationships for classes and groups of classes of the chemicals. Measured acute toxicities to Daphnia pulex and regressions of toxcities on several properties obtained from the QSAR data base are presented in TABLES 1 and 2. Equations (4), (6), (8), and (10) of TABLE 2 are graphed in FIGURES 1 to 4.

Initial QSAR regression lines included all data. However, certain data were excluded from equations (4) to (11) of TABLE 2 because of problems with either the QSAR estimates or with the bioassays. I did not exclude data because of suspected lack of fit to a narcosis model. The water solubilities for four heterocyclic nitrogen compounds--nicotine; 2-pyridineethanol; 1-methylpyrrolidine; and 2-amino-4,7(1H,8H)-pteridinedione--and an additional nitrogen-containing compound (1-butylimidazole) ranged from 30,900 to 7,450,000 uM. Because these compounds with high solubilities were generally outliers (possibly because they were acting by a receptor-specific mode of action), I omitted them (on a statistical basis) from regressions of EC50 on water solubility, log P, and log QSAR LC50. Inasmuch as the water solubilities of three silicon-containing compounds--(dodecyloxy)trimethysilane); (decyloxy)trimethylsilane; and siloxytrimethylcyclohexene--were 1.5 to 4 orders of magnitude below the measured acute toxicities, I considered the acute toxicities questionable and excluded them from the regressions. However, the influence of the carrier solvent, acetone, may have increased the solubility of these compounds. It is also possible that these silicon-containing compounds do not act according to a narcosis model. Predicted acute toxicities to *Daphnia* (QSAR LC50) were unavailable for six other chemicals; however, predicted toxicities to fathead minnows (*Pimephales promelas*) were available for three of these so I substituted these values, since QSAR toxicities for *Daphnia* and fathead minnows usually differed by only about 20% (QSAR data base from USEPA, Duluth, MN).

The above examples illustrate the importance of examining QSAR predictions for reasonableness before using them to establish regression equations or before substituting them into established regression equations to predict toxicity. QSAR data bases should be screened to eliminate values such as water solubilities of 1,000,000 $mg.L^{-1}$. Regression equations should be examined for outliers and the chemical or biological basis for statistical outliers considered.

Multiple regression analysis of log EC50 (μM) as a function of the four independent variables (TABLE 2) indicated that 76% of the variation could be explained by a regression on water solubility and molecular volume (Equation 12). The fit was not improved significantly ($\underline{P} > 0.05$) by adding log P and log QSAR LC50 (μM). Water solubility was the single most important independent variable, explaining 71% of the variation (Equation 8).

To examine differences between classes (TABLE 3), I determined that the slopes for all classes were homogeneous. For classes with different intercepts,regressions for individual classes might yield a more accurate predicted EC50, although the regression coefficient could decrease because of the smaller sample size.

Although toxicity is often correlated with log P by a simple linear regression, I examined the quadratic equation that includes the $(\log P)^2$ term, based on the generalized equation of Hansch (Könemann 1981). A plot of the residuals for the simple linear regression showed that the residuals were not randomly distributed, thus violating an assumption of the validity of the simple linear regression. Some investigators have approached the problem of nonlinearity by limiting the equation to log P values below some arbitrary value such as 5 or 6 (Könemann and Leeuwen 1980). When I eliminated toxicants with $\log P \geq 6$, the regression coefficient was lowered ($r^2 = 0.43$). The quadratic equation proved more satisfactory. The following regression was calculated with the same 26 data points from Equation 6:

$$\log \mathrm{EC50}(\mu\mathrm{M}) = -2.47 + 3.60 \log P - 0.58 (\log P)^2 \qquad (14)$$

$n = 26;\ r^2 = 0.77;\ s = 1.29$

The regression coefficient (r2 = 0.77) improved over the value (r^2 = 0.69) for equation 6. A plot of the residuals of equation 14 indicated a random distribution, thus supporting the assumption that the quadratic equation is a valid model. Equation 14 describes a nonlinear relation in which the toxicity reaches a maximum (FIGURE 5). The biological basis for this curve may be that increased lipophilicity favors transport of the toxicant into the membrane and to target sites up to a certain optimum lipophilicity, as measured by log P, after which point, with increased lipophilicity, the toxicants are sequestered in the membrane and tend less to reach the target sites.

TABLE 4 presents the acute toxicity values of 18 solutes (TABLE 1) to Daphnia pulex and the intrinsic molecular volume and solvatochromic terms for solutes for which values of $V_I/100$, π^*, α_m, and β_m are known or can be estimated. The multiple linear regression for the 18 solutes in TABLE 4 is given by the following equation:

$$EC50(\mu M) = 12.1 - 10.7\ V_I/100 - 2.46\ \pi^* + 6.62\ \beta_m \qquad (15)$$

$$n = 18;\ r = 0.9199;\ s = 0.85$$

The hydrogen bonding donor acidity term α_m was not significant for this data set. By standards that Kamlet (1986a) applied to other QSAR correlations of equation 2--even if not necessarily by the standards usually applied to correlations of biological properties--the r and SD values of equation 15 represent unsatisfactory goodness of fit. I therefore undertook to examine the outliers in the correlation to ascertain whether nonconformance with equation 15 is due to reactive toxicological behavior, as opposed to nonreactive behavior of solutes fitting a narcosis model. After solutes 5, 11, 16, and 17 were dropped, the new regression for 14 solutes from TABLE 4 was as follows:

$$EC50(uM) = 13.9 - 12.7\ V_I/100 - 4.30\pi^* + 15.6\ \beta_m \qquad (16)$$

$$n = 14;\ r = 0.9763;\ s = 0.51$$

This equation shows that increasing solute intrinsic molecular volume and decreasing solute HBA basicity, which lead to lower solubility in water, also lead to greater toxicity (lower EC50 values) of the toxicants, but that higher solute dipolarity/polarizability (π*), which leads to greater solubility in water, also leads to lower EC50 values. Kamlet et al. (1986a;1986b) observed similar converse effects of solute dipolarity on toxicities to luminescent bacteria and golden orfe fish and feel these observations may have important implications regarding the mechanism of toxicity or narcosis.

Besides correlating QSAR parameters with measured toxicity, Passino and Smith (1986) qualitatively compared measured toxicity with the presence of functional groups on the molecules. Although they tested only 2 to 13 chemicals in each class, certain relations were suggested. The presence and position of methyl groups on PAHs were related to toxicity--e.g., the 48-h EC50 ($mg.L^{-1}$) for naphthalene was 4.66, compared with 0.193 for 2,6-dimethylnaphthalene and 0.506 for 1,3-dimethylnaphthalene (TABLE 1). The most toxic compound--aside from the reference chemical p,p'DDT, which is recognized to act by specific reactive toxicological behavior--was 1,4,9,9-tetramethyloctahydromethanoazulene, which had a bridge carbon as well as four methyl groups. The toxicity of alkyl halides appeared to depend on the particular halide attached (Cl > Br > I), chain length (longer-chain compounds were more toxic than shorter-chain compounds), and branching of the chains--e.g., 2-iodobutane was less toxic than 2-iodo-2-methylpropane.

Regression equations, taken together with considerations of the presence and position of key functional groups predicted the acute toxicity of PAHs, alkyl halides, cyclic alkanes, and heterocyclic nitrogen compounds to *Daphnia pulex* by classical QSAR models. Values for parameters for the solvatochromic model were lacking for these heterocyclic nitrogen compounds. Verification of the relation between acute toxicities to *Daphnia* and those to fish for chemicals in these classes is needed. Because of possible reactive modes of action, low solubility, or both, Passino and Smith (1986) were not able to apply the QSAR models to silicon-containing compounds or other nitrogen-containing compounds. The regressions discussed in this paper have application to hazard assessment of chemicals that are detected and confirmed as present in fish and other aquatic biota. Although QSAR models for hazard assessment are still primarily a research tool, they should become useful to operations personnel after further development of larger aquatic toxicity data sets to verify the models and further work on the toxicological basis for the models.

ACKNOWLEDGMENTS

I thank Anthony M. Frank for guidance with biometrics, SAS programs, and computer graphics; Dr. Mortimer J. Kamlet, Naval Surface Weapons Center, White Oak Laboratory, Silver Spring, Maryland, for introducing me to linear solvation energy relationship; and Marc A. Blouin, Cynthia M. Perry-Sayers, Dr. Jacqueline F. Savino, and Stephen B. Smith for laboratory bioassays.

REFERENCES

Baumann, P.C. 1984. Cancer in wild freshwater fish populations with emphasis on the Great Lakes. J. Great Lakes Res. 10:251-253.

Crum Brown, A. and Fraser, T.R. 1868-1869. On the connection between chemical constitution and physiological action. I. On the physiological action of salts of the ammonium bases, derived from strychnia, brucia, thebaia, codeia, morphia, and nicotia. Trans. R. Soc. Edinburgh 25:151-203 (not seen; cited by Dearden 1985).

Dearden, J.C. 1985. Partitioning and lipophilicity in quantitative structure-activity relationships. Environ. Health Perspect. 61:203-228.

Hansch, C. 1971. Quantitative structure-activity relationships in drug design. In E. J. Ariens, ed., Drug Design, vol. 1, pp. 271-342. Academic Press, New York.

Hansch, C. and Fujita, A. 1964. Rho, sigma and pi analysis-correlations of biological activity and chemical structure. J. Amer. Chem. Soc. 86:1616-1626.

Hesselberg, R.J. and Seelye, J.G. 1982. Identification of organic compounds in Great Lakes fishes by gas chromatography/mass spectrometry: 1977. Administrative Report No. 82-1. Great Lakes Fishery Laboratory, Ann Arbor, Michigan.

Kaiser, K.L.E. 1984. QSAR in Environmental Toxicology. D. Reidel, Dordrecht, Holland.

Kamlet, M.J., Doherty, R.M., Veith, G.D., Taft,R.W. and Abraham,M.H. 1986a. Solubility properties in polymers and biological media. 7. An analysis of toxicant properties that influence inhibition of bioluminescence in Photobacterium phosphoreum (the Microtox test). Environ. Sci. Technol. 20:690-695.

Kamlet, M.J., Doherty, R.M., Taft, R.W., Abraham, M.H., Veith, G.D. and Abraham, D.J. 1986b. Solubility properties in polymers and biological media. 8. An analysis of the factors that influence toxicities of nonelectrolytes to the golden orfe fish (Leuciscus idus melanotus). Environ. Sci. Technol. In press.

Kamlet, M.J., Doherty, R.M., Abboud, J.-L.M., Abraham, M.H. and Taft, R.W. 1986c. Linear solvation energy relationships: 36. Molecular properties governing solubilities of organic nonelectrolytes in water. J. Pharm. Sci. 75:338-349.

Könemann, H. 1981. Quantitative structure-activity relationships in fish toxicity studies. Part 1: Relationship for 50 industrial pollutants. Toxicology 19:209-221.

Könemann, H. and Leeuwen, K. van. 1980. Toxicokinetics in fish: Accumulation and elimination of six chlorobenzenes by guppies. Chemosphere 9:3-19.

Mac, M.J., Edsall, C.C. and Seelye, J.G. 1985. Survival of lake trout eggs and fry reared in water from the upper Great Lakes. J. Great Lakes Res. 11:520-529.

Meyer, H. 1899. Lipoidtheorie der Narkose. Arch. Exp. Pathol. Pharmakol. 42: 109-118 (not seen; cited by Dearden 1985).

Moriguchi, I., Kanada, Y. and K. Komatsu. 1976. Van der Waals volume and the related parameters for hydrophobicity in structure-activity studies. Chem. Pharm. Bull. 24:1799-1806.

National Fisheries Center-Great Lakes. 1986. Progress in Fishery Research 1984-1985. U.S. Fish and Wildlife Service, National Fisheries Center-Great Lakes, Ann Arbor, Michigan.

Neely, W.B., Branson, D.R. and Blau, G.E. 1974. Partition coefficient to measure bioaccumulation potential of organic chemicals in fish. Environ. Sci. Technol. 8:1113-1115.

Overton, E. 1901. Studien über die Narkosen. Gustav Fisher, Jena, Germany.

Passino, D.R.M., Hesselberg, R.J. and Willford, W.A. 1986. Preliminary identification and hazard ranking of 476 organic compounds in Great Lakes fishes. J. Great Lakes Res. In press.

Passino, D.R.M. and Novak, A.J. 1984. Toxicity of arsenate and DDT to the cladoceran Bosmina longirostris. Bull. Environ. Contam. Toxicol. 33: 325-329.

Passino, D.R.M. and Smith, S.B. 1986 Quantitative structure-activity relationships (QSAR) and toxicity data in hazard assessment. In K.L.E. Kaiser, ed., QSAR in Environmental Toxicology. D. Reidel, Dordrecht, Holland. In press.

Perry, C.M. 1985. The toxicological effects of six heterocyclic nitrogen compounds on Daphnia pulex. M.S. Thesis, Eastern Michigan University, Ypsilanti, Michigan.

SAS Institute Inc. 1985. SAS Users Guide: Basics, Version 5 Edition. SAS Institute Inc., Cary, North Carolina.

TABLE 1. Chemicals used for calculating QSAR equations. Acute toxicity to Daphnia pulex (National Fisheries Center-Great Lakes 1986). Water solubility (calculated values from QSAR data base of U.S. Environmental Protection Agency, Duluth, MN). From Passino and Smith (1986).

Chemical	CAS No.	Formula	48-h EC50 µM	Water solubility µM
Cyclohexane,bromo-	108850	$C_6H_{11}Br$	36.6	508
Decane,1-bromo-	112298	$C_{10}H_{21}Br$	0.335	0.89
Dodecane,1-chloro-	112527	$C_{12}H_{25}Cl$	0.0644	0.07
Butane,2-iodo-	513484	C_4H_9I	59.2	1470
Cyclohexane,chloro-	542187	$C_6H_{11}Cl$	34.1	1040
Hexadecane,1-iodo-	544774	$C_{16}H_{33}I$	0.702	0.00
Nonane,1-bromo-	693583	$C_9H_{19}Br$	2.61	3.60
Cyclohexane,(3-chloro-1-propnyl)-	55723994	$C_9H_{13}Cl$	10.1	660
Cyclopentane,propyl-	2040962	C_8H_{16}	27.8	26.0
Cyclohexane,1,2-dimethyl-,cis-	2207014	C_8H_{16}	28.9	24.6
Cyclohexane,1,2-dimethyl-,trans-	6876239	C_8H_{16}	43.5	24.6
Pinane,-trans-	10281535	$C_{10}H_{18}$	24.3	11.4
Pyridine,3-(1-methyl-2-pyrrolidinyl)- [Nicotine]	54115	$C_{10}H_{14}N_2$	1.50	141000
2-Pyridineethanol	103742	C_7H_9ON	112	7450000
Pyrrolidine,1-methyl-	120945	$C_5H_{11}N$	24.5	569000
4,7(1H,8H)-Pteridinedione,2-amino-	529691	$C_6H_5O_2N_5$	16.40	
Imidazole,1-butyl-	4316421	$C_7H_{12}N_2$	53.0	30900
Phenanthrene	85018	$C_{14}H_{10}$	1.97	6.57
Fluorene	86737	$C_{13}H_{10}$	1.28	9.76
Decalin	91178	$C_{10}H_{18}$	18.0	14.4
Naphthalene	91203	$C_{10}H_8$	36.4	230
Tetralin	119642	$C_{10}H_{12}$	18.2	113
Anthracene	120127	$C_{14}H_{10}$	4.24	0.607
Hydrindan	496106	C_9H_{16}	29.8	39.7
Naphthalene,1,3-dimethyl-	575417	$C_{12}H_{12}$	4.92	22.9
Naphthalene,2,6-dimethyl-	581420	$C_{12}H_{12}$	1.24	4.08
Anthracene,2-methyl-	613127	$C_{15}H_{12}$	0.502	1.46
Naphthalene,decahydro-2,3-dimethyl-	1008806	$C_{12}H_{22}$	0.242	0.436
Anthracene,9-methoxy-	2395962	$C_{15}H_{12}O$	1.90	572
1H-3A,7-Methanoazulene,1,4,9,9-tetramethyloctahydro-	19078354	$C_{15}H_{26}$	0.0182	0.199
p,p'DDT	50293	$C_{14}H_9Cl_5$	0.00299	0.00876
Silane,dimethyldiethyoxy-	78626	$C_6H_{16}O_2Si$	17.9	42.1
Silane,(dodecyloxy)trimethyl-	6221881	$C_{15}H_{34}OSi$	0.703	0.0001
Cyclohexene,siloxytrimethyl-	6651361	$C_9H_{18}OSi$	289	
Silane,(decyloxy)trimethyl-	18402103	$C_{13}H_{30}OSi$	25.3	0.0035

TABLE 2. Summary of structure-activity regressions of measured acute toxicity of PAHs, alkyl halides, cyclic alkanes, and heterocyclic nitrogens to *Daphnia pulex* (EC50)[a] with several QSAR calculated properties of the chemicals; where QSAR LC50 = calculated toxicity to *Daphnia*; C_w = water solubility; MV = molecular volume; and the units are indicated as μM or $mg \cdot L^{-1}$; s = the square root of the mean square error for regression. From Passino and Smith (1986).

Equation No.	Equation
(4)	$\log EC50(\mu M) = 0.59 + 0.693 \log QSAR\ LC50(\mu M)$
	$n = 23;\ r^2 = 0.44;\ s = 1.41$
(5)	$\log EC50(mg \cdot L^{-1}) = 0.0192 + 0.609 \log QSAR\ LC50(mg \cdot L^{-1})$
	$n = 23;\ r^2 = 0.38;\ s = 1.35$
(6)	$\log EC50(\mu M) = 10.5 - 2.03 \log P$
	$n = 26;\ r^2 = 0.69;\ s = 1.48$
(7)	$\log EC50(mg \cdot l^{-1}) = 8.05 - 1.89 \log P$
	$n = 26;\ r^2 = 0.70;\ s = 1.33$
(8)	$\log EC50(\mu M) = -0.539 + 0.714 \log C_w(\mu M)$
	$n = 26;\ r^2 = 0.54;\ s = 1.28$
(9)	$\log EC50(mg \cdot L^{-1}) = -1.04 + 0.674 \log C_w(mg \cdot L^{-1})$
	$n = 26;\ r^2 = 0.68;\ s = 1.39$
(10)	$\log EC50(\mu M) = 9.15 - 0.0448\ MV$
	$n = 32;\ r^2 = 0.63;\ s = 1.54$
(11)	$\log EC50(mg \cdot L^{-1}) = 6.65 - 0.0410\ MV$
	$n = 32;\ r^2 = 0.63;\ s = 1.43$
(12)	$\log EC50(\mu M) = 3.72 + 0.485 \log C_w(\mu M) - 0.0208\ MV$
	$n = 26;\ r^2 = 0.76;\ s = 1.32$
(13)	$\log EC50(mg \cdot L^{-1}) = 2.89 + 0.435 \log C_w(mg \cdot L^{-1}) - 0.0213\ MV$
	$n = 26;\ r^2 = 0.75;\ s = 1.24$

---

[a] From National Fisheries Center-Great Lakes 1986.

TABLE 3. Summary of covariance tests for differences between classes for the structure-activity regressions between log EC50(μm) and several independent variables (see TABLE 1). Lines under classes indicate no significant differences for intercepts, where Het. N = heterocyclic nitrogens, Alk.X = alkyl halides, Cy. Alk. = cyclic alkanes. From Passino and Smith (1986).

Independent variable	Class differences[a]		Classes sorted
	Slope	Intercept	$P \geq 0.05$
log QSAR (μM)	NS	*	Alk.X PAHs Cy.Alk.
log P	NS	*	PAHs Alk.X Cy.Alk.
log C_w(μM)	NS	*	Alk.X PAHs Cy.Alk.
MV	NS	**	PAHs Het.N Alk.X Cy.Alk.

---

[a] NS = not significant $P > 0.05$

* = $P \leq 0.05$

** = $P \leq 0.01$

TABLE 4. Data used in correlation of non-reactive toxicological effects on Daphnia pulex with intrinsic molecular volume and solvatochromic parameters.

No.	Toxicant	$V_I/100$	π^*	β_m	log EC50 μM
1	Phenanthrene	1.015	0.80	0.20	0.68
2	Naphthalene	0.753	0.70	0.15	3.59
3	2-Methylnaphthalene	1.113	0.76	0.21	-0.69
4	1,3-Dimethylnaphthalene	0.949	0.62	0.17	1.59
5	2,6-Dimethylnaphthalene	0.949	0.62	0.17	0.21
6	Tetralin	0.883	0.50	0.12	2.91
7	9-Methoxyanthracene	1.153	0.93	0.32	0.64
8	Anthracene	1.015	0.80	0.20	1.44
9	Fluorene	0.900	1.00	0.20	0.24
10	1-Chlorododecane	1.324	0.26	0.10	-2.74
11	1-Bromononane	1.079	0.35	0.05	0.96
12	1-Bromodecane	1.177	0.34	0.05	-1.09
13	Propylcyclopentane	0.794	0.02	0	3.37
14	Dimethylcyclohexane	0.794	0.02	0	3.57[a]
15	Hydrindan	0.884	0.02	0	3.40
16	Decalin	0.982	0.03	0	2.89
17	Chlorocyclohexane	0.688	0.35	0.10	3.53
18	Dimethyldecahydro naphthalene	1.180	0.03	0	-1.42

[a] Mean of cis and trans isomers

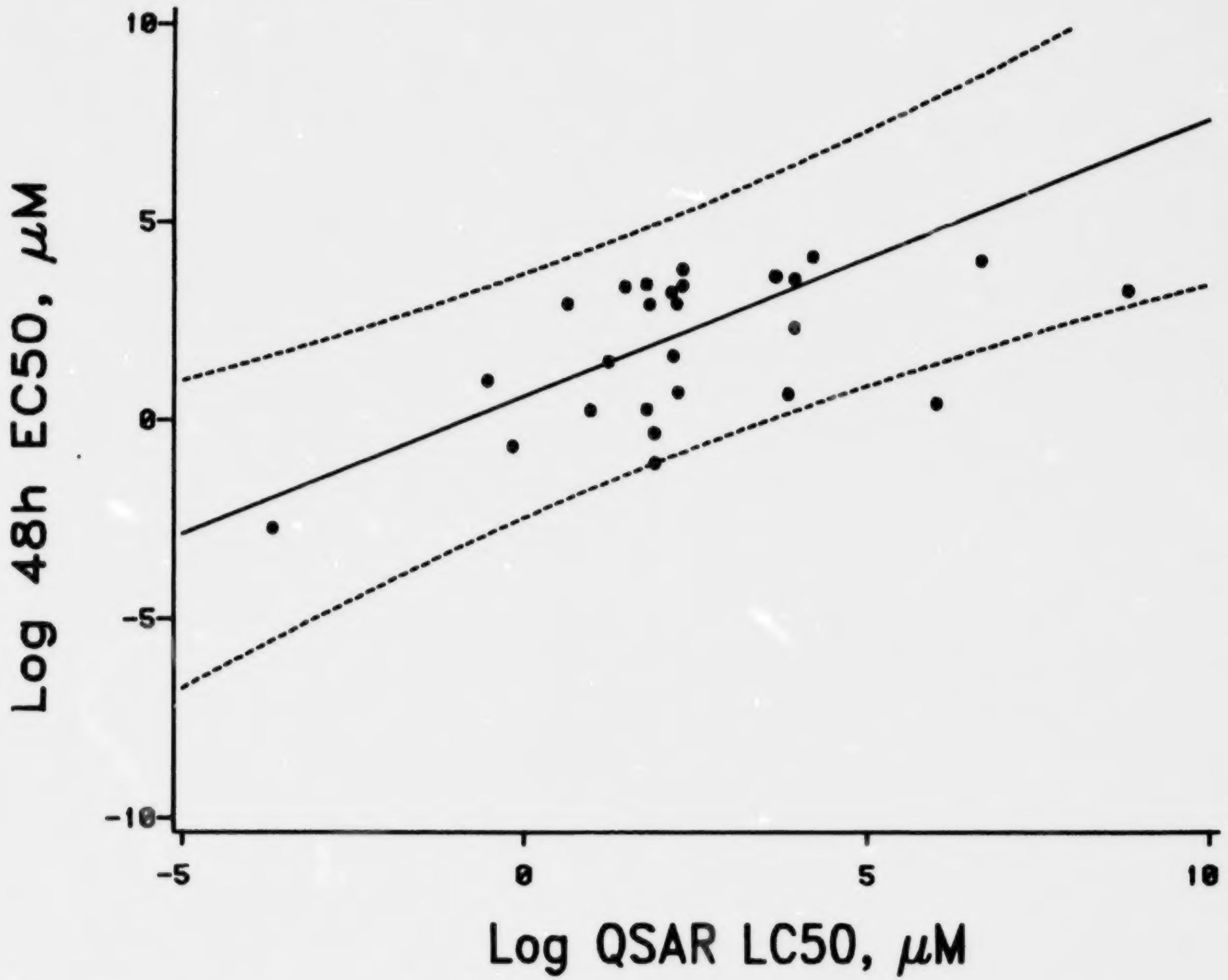


FIGURE 1. Measured acute toxicity to Daphnia pulex of six classes of chemicals versus calculated acute toxicity to Daphnia by QSAR (see TABLE 1).

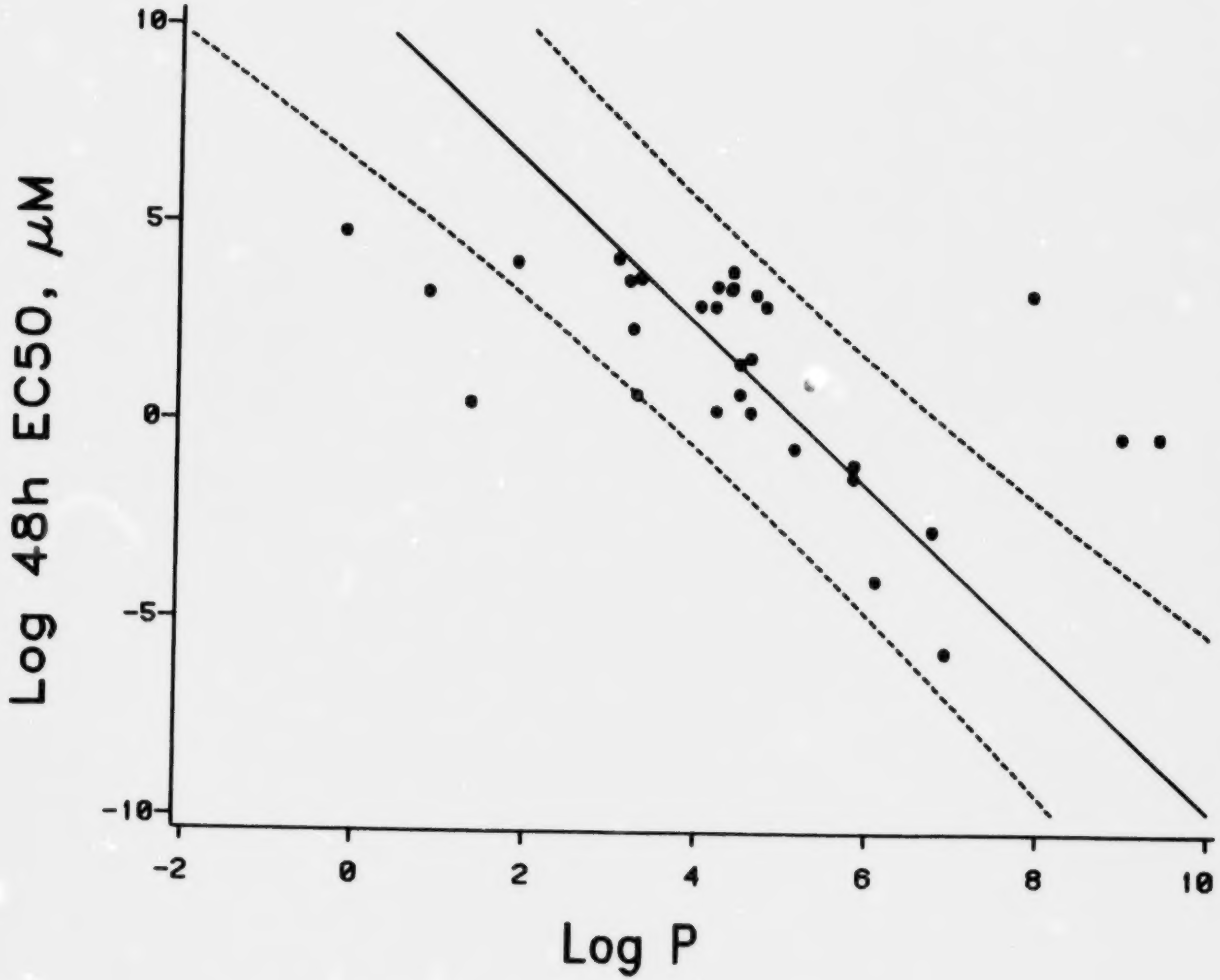


FIGURE 2. Measured acute toxicity to *Daphnia pulex* of six classes of chemicals versus calculated log P by QSAR (see TABLE 1).

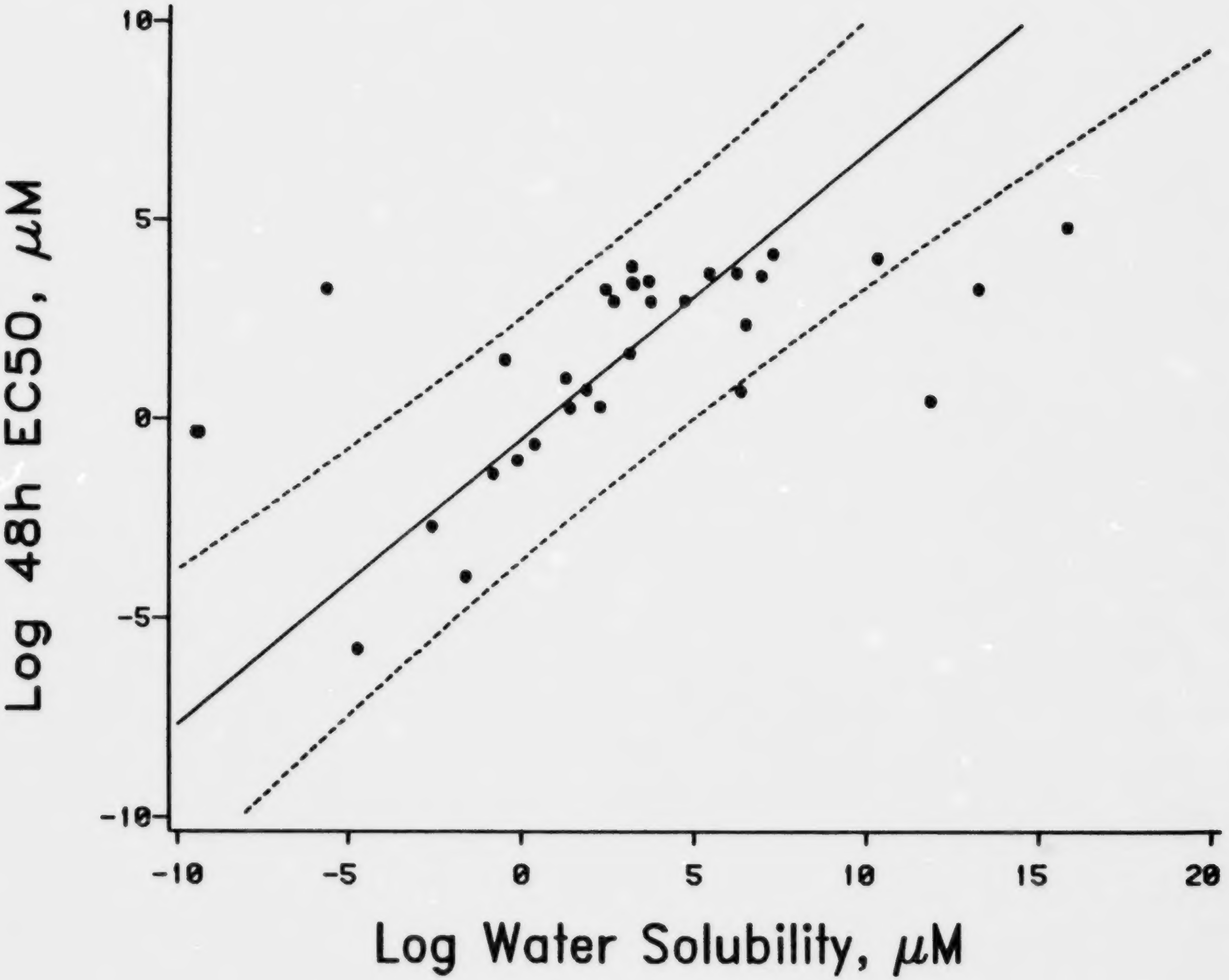


FIGURE 3. Measured acute toxicity to Daphnia pulex of six classes of chemicals versus calculated water solubility by QSAR (see TABLE 1).

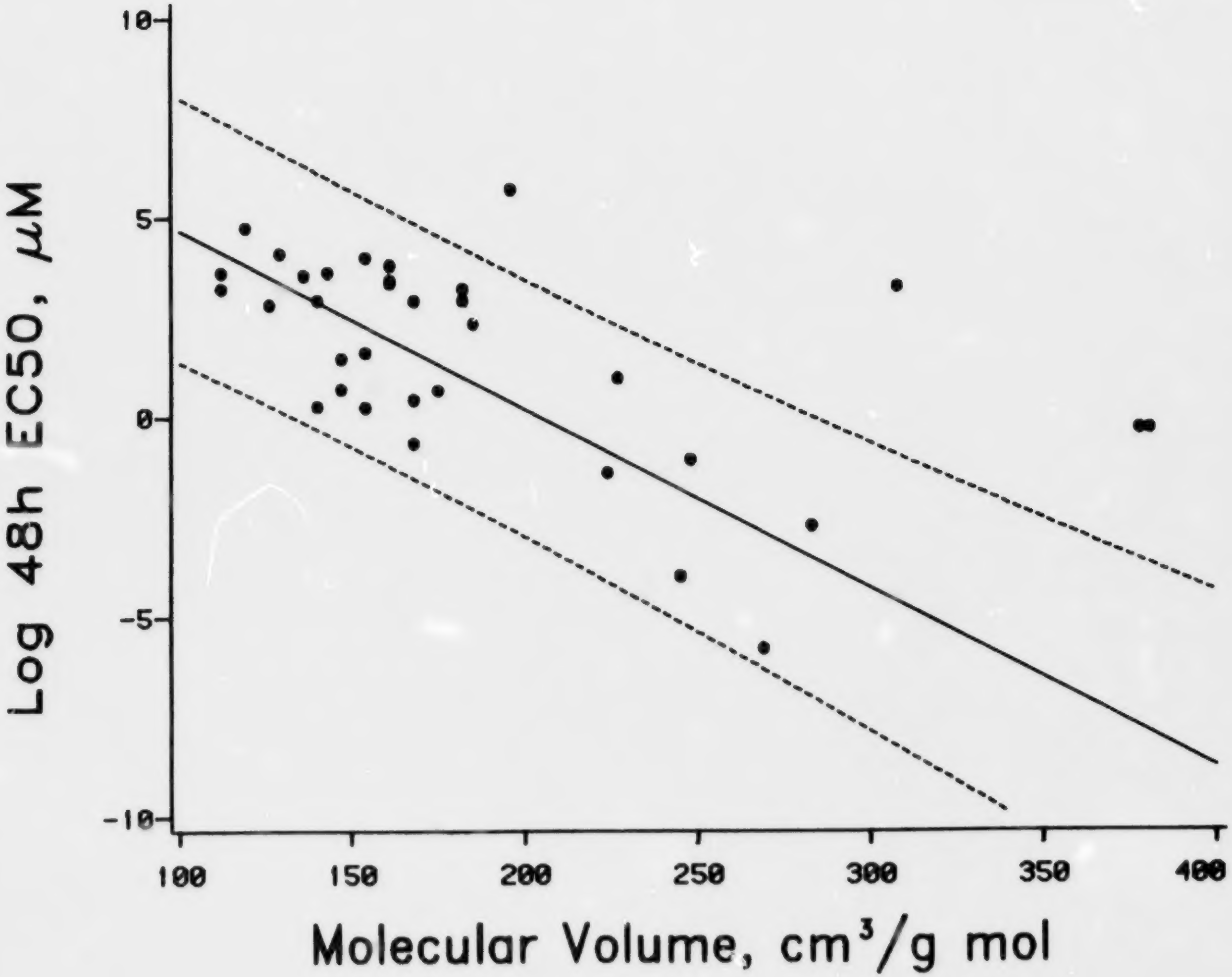


FIGURE 4. Measured acute toxicity to *Daphnia pulex* of six classes of chemicals versus calculated molecular volume by QSAR (see TABLE 1).

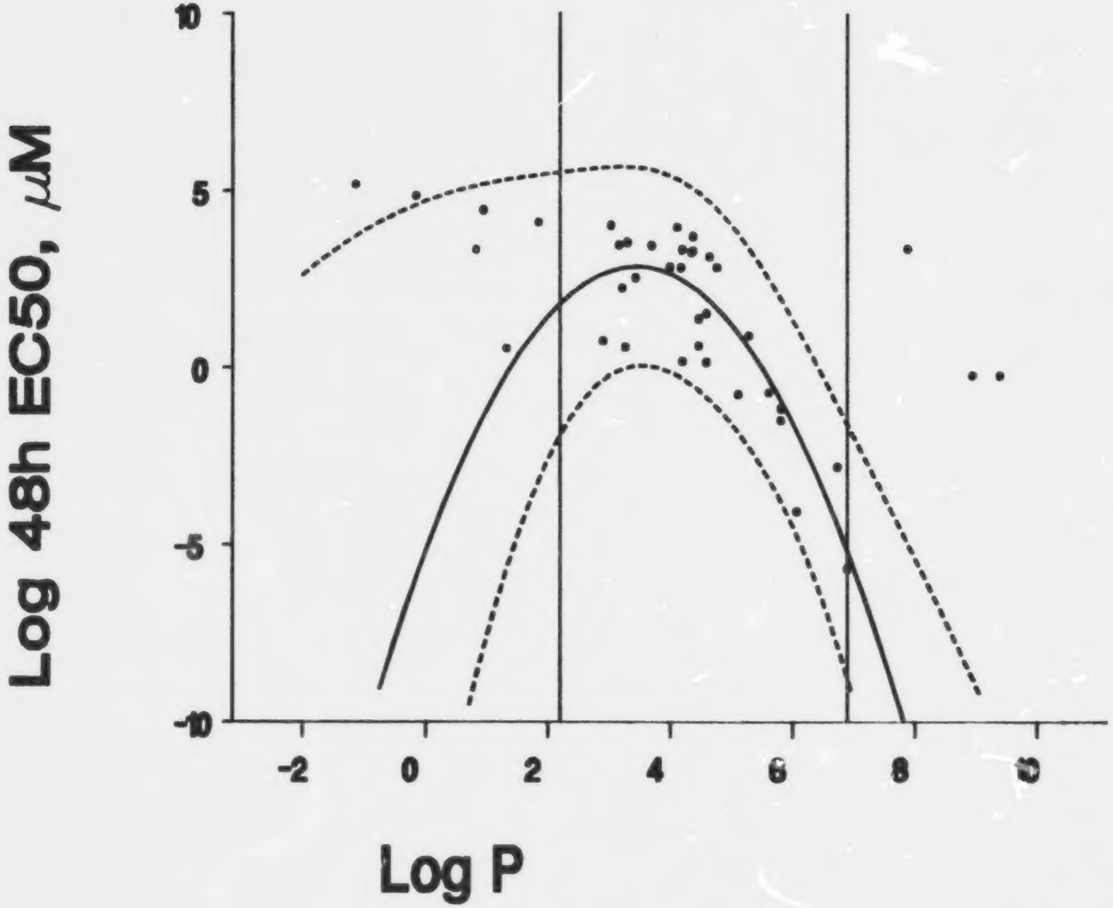


FIGURE 5. Measured acute toxicity to *Daphnia pulex* of six classes of chemicals versus calculated Log P by QSAR (see TABLE 1). The vertical lines approximately delineate the range within which the data points were used for the regression.

CONTROL OF TOXIC TRACE CONTAMINANTS IN MUNICIPAL WASTEWATER TREATMENT PLANTS

Henryk Melcer
Wastewater Technology Centre
Environment Canada
Burlington, Ontario

Ontario Ministry of Environment
Technology Transfer Conference
Toronto, Ontario
8-9 December, 1986

CONTROL OF TOXIC TRACE CONTAMINANTS IN MUNICIPAL WASTEWATER TREATMENT PLANTS

ABSTRACT

Data from more than one hundred municipal wastewater treatment plants were reviewed to determine the most frequently occurring organic and inorganic trace contaminants in treated effluents. Typically, these were volatile chlorinated compounds, phthalate esters and metals. They were found to be removed by volatilization, biodegradation or possibly by adsorption. Manipulation of solids retention time was observed to be a viable approach to controlling the discharge of toxic trace contaminants from sewage treatment plant effluents.

INTRODUCTION

Several major studies were initiated in the late 1970s to measure the removal of trace contaminants in municipal wastewater treatment plants. The U.S. Environmental Protection Agency (USEPA) commissioned the 40 POTW (Publicly-Owned Treatment Works)(1) and the 25 POTW(2) surveys. Although not as large, early Canadian surveys included the St. Clair River Study by the Ontario Ministry of the Environment (MOE)(3) and the Environment Canada (EC) Toxics Study of the Cornwall and Niagara River area municipal wastewater treatment plants(4). Typically, ten to fifteen USEPA priority pollutants were found in effluents from biological wastewater treatment plants at relatively low concentrations of 10 to 30 μg/L.

At about the same time, the need for utilizing solids retention time (SRT) control strategies for controlling the removal of trace contaminants in biological wastewater treatment plants was recognized by the scientific community. Manipulation of SRT allowed the treatment plant operator to have control of the microbial growth rate. Key slow-growing organisms that were thought to be responsible for attacking complex molecules could be retained in the biomass. Therefore, provision existed, through SRT control, for addressing those contaminants that were difficult to degrade.

Despite the evidence that trace contaminants were not as prevalent as was originally anticipated, and, that measures existed to control those contaminants that were present in municipal wastewaters, the issue of contaminant emissions continued to receive considerable attention. In Ontario, this can be explained, in part, by our close proximity to the Niagara River and its attendant publicity regarding the discharge and disposal of toxic chemicals. Also, the last five years have seen the introduction of better analytical techniques that have the capability of measuring increasingly lower concentrations of organic compounds in aqueous systems. This relative improvement in measurement has refocussed attention on the incidence of toxic trace contaminants in discharges to the Great Lakes. Finally, there has been a rapidly growing public awareness of the fate of anthropogenic compounds and the impact that they may have on our health and the status of the ecosystem. Consequently, not only have further performance assessments been carried out but also many studies have addressed fate of contaminants in municipal sewage treatment plants (STPs). Accordingly, this paper reviews the status of toxic trace contaminant removal in STPs since the time of the landmark surveys of the early 1980s, to those which are currently in progress. Also, studies on the fate of contaminants in biological treatment systems are reviewed.

COMPARATIVE ANALYSIS OF TRACE CONTAMINANT DATA

The majority of data collected to demonstrate the performance of municipal STPs is based on the 126 USEPA priority pollutants. This practice stems from the 1976 consent decree on priority pollutants when the emphasis in the Clean Water Act for water pollution control in the U.S. shifted from regulation based on conventional pollutants alone to regulation based upon conventional and specific toxic pollutants. Considerable analytical chemical methodology development was undertaken to provide protocols that would address those contaminants that were legislated by the Clean Water Act, that is, the priority pollutants. Since that time, it has become evident that many of the priority pollutants are biodegradable and can be removed in municipal STPs. On the other hand, it has also been observed that many commonly used solvent, pesticide and plasticizer chemicals demonstrate toxic and persistent qualities, but are not included in the list of priority pollutants. They have not been addressed in monitoring or screening procedures until recently, because of the expensive and time-consuming analytical protocol development required to generate methods that are easy to use and give reproducible data. Thus despite the fact that many lists of priority or suspect chemicals have been prepared by regulatory agencies, the most actively reported is that of the USEPA priority pollutants.

There are several reasons why meaningful comparison of data from different surveys is difficult. These include the circumstances under which samples were collected, sampling frequency, method of data reporting and method of sample analysis.

Knowledge of the process operating conditions is very valuable when comparing trace contaminant removal data. This is especially true when comparing laboratory or pilot scale data with field data. The removal of trace contaminants can be affected by the level of biomass acclimation before the commencement of the study. Contaminant removal may also be affected by the method of substrate feed, single or multiple, and by the degree of equilibrium achieved during a study. Other important process considerations are the system hydraulic retention time (HRT), SRT, level of aeration and the feed contaminant concentration. In some cases, the difficulty in comparing removal efficiencies is exacerbated by the presence or absence of chlorination in the treatment sequence. Chlorinated effluents often have elevated concentrations of chlorinated species such as methylene chloride and chloroform. Therefore, removals of these contaminants are often reported as zero or negative. It is rare for researchers to record whether chlorinated or unchlorinated effluent samples were analyzed.

Sampling frequency is not consistent between studies. This discrepancy is often due to the high cost of trace contaminant analysis. Data have been reported based on a single annual sample, on monthly determinations, or, a short series of daily values. The chemical analysis may be carried out on a single grab sample or on a flow-proportioned 24 hr composite sample. Data are then reported as arithmetic or geometric means and medians without any indication whether the values have been corrected for recoveries or not. Various types of probability distribution functions may be fitted to effluent quality data but no single type has been suitable for all plants. The log-normal distribution is the one that provides an adequate fit most often (5). Sludges may be reported on a wet weight or dry weight basis with no data on the corresponding solids concentration. Execution of a meaningful comparison of statistics is difficult under such circumstances.

The technology of trace contaminant analysis has advanced rapidly during this decade. Levels of detection have been decreasing steadily. As a result of analytical limitations, earlier performance assessments have more values reported as non detected. They were regarded as being zero, or were assigned a value equivalent to the detection level or a value midway between zero and the detection level. Different conclusions may be drawn depending upon how these values were assigned. Although technology has improved the ability to detect contaminants at very low concentrations, there is an inherent difficulty in evaluating contaminant removal efficiencies. This results from the level of uncertainty that still exists with measurement at concentrations near detection limits and leads to considerable variability in effluent data. Conversely, there is difficulty in the measurement of contaminants in influent samples which is attributed to the presence of extraneous organic matter. This organic matrix can interfere with the extraction efficiency of the methylene chloride solvent used to extract the priority pollutants from wastewater samples. This phenomenon can produce a high level of variability in influent contaminant data.

PERFORMANCE ASSESSMENT OF MUNICIPAL STPs FOR REMOVAL OF TOXIC TRACE CONTAMINANTS

Little is known about the human toxicological effect of discharging trace contaminants in STP effluents. The most conservative control strategy possible has been taken in which the lowest concentration of trace contaminants technically achievable is sought. There are limited resources available to address the removal of trace contaminants from STP effluents. Therefore, priorities must be set to utilize these resources in the most cost effective manner. The contaminants that exist in treated effluents pose a greater potential environmental threat to receiving waters than those in raw wastewaters and, therefore, examination of effluent constituents would appear to warrant a greater priority than an assessment of raw wastewater constituents.

In this review of trace contaminant removal data, attention has been focussed on the USEPA priority pollutants because they form the largest group of trace contaminant data that exists in the literature. An arbitrary basis of comparison was selected, data permitting, in which mean effluent characterization data are presented for those compounds that occurred at concentrations in excess of 1.0 μg/L for more than 50% of the time. A limited number of chlorinated species such as pesticides and PCBs, if they are present, occur generally at much lower concentrations, at one to two orders of magnitude lower than the 1.0 μg/L basis of comparison. Therefore, they are not addressed in this review.

True removal data are difficult to estimate in view of the organic matrix effect on influent sample analysis, the effect of chlorination on effluent constituents and the relative inaccuracy of measurement at detection limits for effluent samples. Therefore, removal data are not presented in this review. Instead, mean influent concentration data are given for the most frequently occurring effluent contaminants for comparison purposes.

On a cautionary note, the protocols used for USEPA priority pollutant analysis will address up to one percent of the organic content of a wastewater sample, treated or otherwise. Many other organic compounds will be present. They make up the remaining part of the organic content of wastewaters. Much of the organic content is made up of large molecular weight compounds some of which are not well defined and about which little is known of their human toxicological effects. Some compounds, however, will be site specific, their occurrence being related to the presence of specific industries that discharge their wastewaters to the STP.

Landmark Studies

These studies were undertaken by the USEPA to address the toxic chemical control measures as defined by the Clean Water Act. They serve as a useful basis of comparison with more recent work. During the period 1978-1981, the USEPA conducted two surveys of trace contaminant removal in STPs. In the first survey, known as the 25 POTW Study, single 24 hr composite samples were taken of the major streams at 25 secondary STPs(2). In a second, more comprehensive survey, the 40 POTW Study, 24 hr composite samples were collected of the major streams at 40 secondary STPs over a period of six consecutive days(1). In the 40 POTW Study, 27 of the 40 STPs met their 30:30/BOD5:TSS discharge permit during the survey.

Both surveys revealed considerable variability in influent concentrations and removal efficiencies of the individual trace contaminants. Very few of the priority pollutants were found on a regular basis in the final effluents in either study. Seven organic compounds and four metals were found above 1 µg/L at least 50% of the time in the 40 POTW Study (Table 1). Seven organic contaminants were similarly found in the 25 POTW Study. Six were the same as those identified in the 40 POTW Study (Table 1). The seventh was diethyl phthalate which occurred 62% of the time. No metal data were collected in the 25 POTW Study.

The Environment Canada Toxics Study(4) identified five organic contaminants that occurred above 1 µg/L at least 50% of the time (Table 1). Samples were composited over seven days at nine STPs and over 24 hr at six STPs in this study. Phenol was found 73% of the time contrary to either the 25 or the 40 POTW Studies. No metal data were collected in the EC study. In the limited screening of the St. Clair River STPs conducted by the Ontario Ministry of the Environment in 1977, all the volatile contaminants listed in Table 1 were also found in the plant effluents(3).

The STPs in the 40 POTW Study were selected to obtain a cross section of secondary treatment processes identified in the 1978 USEPA Needs Survey. These STPs varied in treatment capacity, influent characteristics and industrial flow

TABLE 1 - CONCENTRATION OF MOST FREQUENTLY FOUND TRACE CONTAMINANTS IN THE 40 POTW STUDY (1)

Contaminant (µg/L)	Influent[1]	**Effluent[2]**
Volatiles		
Chloroform[3][4][5]	7	**2**
Methylene chloride[3][4][5]	38	**20**
Tetrachloroethylene[3][4]	23	**20**
Toluene[4]	27	**10**
1,1,1-Trichloroethane[3]	29	**20**
Base Neutrals		
Bis(2-ethylhexyl)phthalate[3][5]	27	**10**
Di-n-butyl phthalate[3][5]	4	**3**
Metals		
Chromium[5]	105	**22**
Copper[5]	132	**23**
Nickel[5]	54	**38**
Zinc[5]	273	**80**
Inorganics		
Cyanide[5]	249	**100**

---

[1] Median values for the 40 POTW influent averages. All influent values reported below the detection limit were assumed to be zero (extracted from Table 9(1)).

[2] The minimum effluent concentrations achieved in the 40 POTW Study at 50% of the POTWs (interpolated from cumulative distributions of effluents(1)).

[3] In the list of most frequently found contaminants in the 25 POTW Study(2).

[4] In the list of most frequently found contaminants in the Environment Canada Toxics Study(4).

[5] In the list of most frequently found contaminants in the 10 POTW Survey, supplementary to the 40 POTW Study (1).

contributions. A further ten STPs were selected as examples of plants that served one primary industry or industrial category(1). Despite the considerable contribution of contaminants made by the industrial flows to each STP, only one inorganic, four organic and five metal trace contaminants were found above 1.0 µg/L more than 50% of the time in the effluents from these additional STPs (Table 1). Silver was the only one of the ten contaminants that was not the same as those observed in the 40 POTW Study.

Although 50 to 100% removal of some of the priority pollutants was achieved in secondary treatment processes, there were insufficient data to conclude whether this was attributable solely to biodegradation and to what extent adsorption and stripping were significant removal mechanisms. However, some pollutants, such as the polyaromatic hydrocarbons (PAHs), that were not detected in influents, were regularly measured at high levels in corresponding primary and secondary sludges. This suggested that adsorption was taking place and that the sludge was effecting a concentration of the adsorbed compounds. This phenomenon has been documented by Bridle et al.(6)

RECENT PERFORMANCE ASSESSMENTS

Canadian Facilities

An annual inspection of the four Metro Toronto plants is based upon the analysis of grab samples of raw wastewater and final effluent collected at four bi-weekly intervals for each STP. Those contaminants that occurred above 1 µg/L for more than 50% of the time in the final effluent(7) are shown in Table 2. Seven of the twelve organic priority pollutants in Table 2 were common to the 25 and 40 POTW Studies. P-xylene and m-xylene were non-priority organic pollutants that were identified at the Toronto Main and Humber STPs. The STPs were able to effect removals of acid extractable contaminants such as phenol (present in raw wastewaters at concentrations up to 80 µg/L), m-cresol (up to 200 µg/L), and p-cresol (up to 420 µg/L) since they were not detected in the effluents. Neither metal nor conventional plant performance data were collected.

TABLE 2 - CONCENTRATION OF MOST FREQUENTLY FOUND TRACE CONTAMINANTS IN METRO TORONTO STP EFFLUENTS(7)

CONTAMINANT (µg/L)	TORONTO MAIN		NORTH TORONTO		HIGHLAND CREEK		HUMBER	
	Inf.	**Eff.**[1]	Inf.	**Eff.**[1]	Inf.	**Eff.**[1]	Inf.	**Eff.**[1]
Volatiles								
Chloroform[2]	2.5	**5.0**	3.8	**3.1**	2.6	**4.0**	10.7	**5.7**
Methylene chloride[2]	45.1	**15.6**	8.2	**2.6**	14.4	**14.9**	54.8	**16.7**
Tetrachloroethylene[2]	6.6	**L**	ND[3]	**L**	7.9	**11.7**	4.4	**L**
Toluene[2]	139	**L**	1.3	**L**	347	**L**	69.0	**2.4**
1,1,1-Trichloroethane[2]	5.6	**L**	ND	**L**	59.9	**4.5**	23.4	**L**
p-& m-Xylene	63.2	**3.0**	1.8	**L**	53.9	**L**	56.2	**2.7**
Base Neutrals								
1,2-Dichlorobenzene	12.9	**3.0**	9.6	**L**	2.1	**2.1**	8.7	**3.7**
1,4-Dichlorobenzene	11.2	**5.1**	7.0	**1.6**	11.1	**7.0**	17.1	**6.0**
Bis(2-EH)phthalate[2]	134	**37.9**	63.8	**14.0**	69.4	**28.2**	85.5	**16.4**
Diethyl phthalate	10.7	**L**	9.0	**1.8**	17.3	**L**	8.9	**L**
Di-n-butyl phthalate[2]	19.6	**2.1**	1.6	**6.2**	32.6	**1.9**	15.7	**5.7**
Acid Extractables								
2,4-Dimethylphenol	2.7	**3.2**	9.4	**L**	2.0	**L**	ND	**4.4**

---

[1] Mean values for those contaminants present in treated effluents at concentrations greater than 1.0 µg/L for more than 50% of the time. Other values designated L indicate that the contaminant occurred less than 50% of the time. Corresponding influent concentrations are mean values.

[2] In the list of the most frequently found effluent contaminants in both 25 and 40 POTW Studies.

[3] ND - Not detected.

During the period 1981 to 1982, a survey of three Niagara Region STPs was conducted. Sixteen sets of samples were collected for metal analysis; between one to ten were collected for volatile organic contaminant analysis(cited by 8). No conventional plant performance data were collected. A high degree of variability in the data was observed. This was attributed to the limited number of samples and to the fact that so many effluent values were close to detection levels. Contaminants that occurred at more than 1.0 μg/L for more than 50% of the time are presented in Table 3. The three metal contaminants listed in Table 3 were common to the 40 POTW Study (Table 1). Of the ten organic contaminants in Table 3, five were common to both 25 and 40 POTW studies and seven were common to the Metro Toronto Survey. The Welland STP, which is an activated sludge plant, typically had fewer organic contaminants than either the Niagara Falls or the Fort Erie STPs, which are primary treatment facilities. At Fort Erie and Niagara Falls, zinc and cyanide were seen regularly in addition to the ten organic compounds.

Very little data have been published on the performance of primary plants in removing toxic trace contaminants. What data there are, address heavy metal removal and there is a paucity of data on the removal of organic trace contaminants. The USEPA conducted a pilot scale comparative assessment of organic contaminant removal in primary plants (that is, primary sedimentation with and without chemical precipitation compared to primary sedimentation with conventional activated sludge)(9). Considerable pass through of contaminants was observed in the primary plants when compared to the secondary system. The data from the Niagara STPs appear to support this observation. Other work by Petrasek et al.(10) indicated that primary sludges are likely to be sinks for metals and those organic compounds which have a propensity for adsorption. Unfortunately, no Niagara STP sludge samples were collected.

In 1984, a study of the removal of PAHs, metals and selected contaminants in the PCB/pesticide group was conducted at the Hamilton, Ontario STP(11). Metals were found to be present at concentrations ranging from 10 to 90 μg/L in the treated effluent, while PAHs were typically detected in the 0.1 to 0.8 μg/L range and PCB/pesticides in the 0.01 to 0.10 μg/L range.

TABLE 3 - CONCENTRATION OF MOST FREQUENTLY FOUND TRACE CONTAMINANTS IN NIAGARA REGION STP EFFLUENTS(CITED BY 8).

CONTAMINANT (μg/L)	WELLAND		FORT ERIE		NIAGARA FALLS	
	Inf.	**Eff.**[1]	Inf.	**Eff.**[1]	Inf.	**Eff.**[1]
Volatiles						
Benzene	<0.1	**L**	0.2	**2.1**	<0.1	**L**
Chloroform[2] [3]	1.3	**2.4**	9.9	**11**	9.7	**4.6**
1,2-Dichlorobenzene[3]	1.7	**L**	4.1	**5.2**	0.6	**3.1**
Ethyl benzene	0.1	**L**	0.1	**1.2**	<0.1	**L**
Methylene chloride[2] [3]	<5	**8.1**	53	**L**	88	**5.2**
Tetrachloroethylene[2] [3]	0.2	**L**	6.4	**12**	4.3	**1.6**
Toluene[2],[3]	3.0	**L**	12	**10**	0.8	**2.2**
1,1,1-Trichloroethane[2] [3]	0.1	**L**	4.8	**4.3**	0.2	**1.3**
o-Xylene	0.3	**L**	0.3	**2.0**	0.1	**L**
m-Xylene[3]	0.4	**L**	5.0	**3.7**	0.1	**L**
Metals						
Chromium[2]	20	**5.0**	8.0	**6.0**	6	**L**
Copper[2]	54	**67**	30	**20**	50	**33**
Zinc[2]	140	**L**	70	**50**	95	**29**
Inorganics						
Cyanide[2]	0.2	**L**	1.0	**7.0**	40	**16**

---

[1] Mean values for those contaminants present in treated effluents at concentrations greater than 1.0 μg/L for more than 50% of the time. Other values designated L indicate that the contaminant occurred less than 50% of the time. Corresponding influent concentrations are mean values.

[2] In the list of the most frequently found effluent contaminants of both 25 and 40 POTW Studies.

[3] In the list of the most frequently found effluent contaminants in the Metro Toronto STP Survey(8).

A very detailed survey of STP effluent trace contaminants is being conducted in an Environment Canada/Ontario Ministry of Environment (EC/MOE) assessment of the dynamic variability of trace contaminants in raw STP wastewaters and their treated effluents(12). One hundred grab samples of both streams were taken at two hour intervals over eight consecutive days at three Southern Ontario STPs in 1986. They were analyzed for volatile, metal and PAH contaminants. Mean values for those contaminants that were present in treated effluents with mean concentrations greater than 1.0 µg/L are presented in Table 4. These data should be regarded as preliminary in view of the fact that the study is still in progress.

All three STPs were secondary plants which produced good quality effluents as defined by effluent FOC and TSS. Some excess solids were discharged at Galt due to severe rainstorm conditions that occurred during part of the study. All three STPs show a significant presence of metal contaminants. Both Welland and Waterloo had minimal organic contaminants in their effluents which, in part, is corroborated by the Welland data collected earlier (Table 3). The Galt STP effluent contained low concentrations six organic contaminants. Three of these were in the list of the most commonly occurring effluent contaminants in both the 25 and 40 POTW Studies. PAHs were not found in the influents or the effluents at all three STPs.

A joint U.S.-Canadian Survey is underway of the major point source discharges to the waterways between the Great Lakes. Known as the Upper Great Lakes Inter-Connecting Channel Study (UGLCCS), the survey addressed the St. Clair River in 1985. Data have been extracted from this study which are specific to the STPs that were sampled at that time(13). Between three and seven composite samples were taken of influents and effluents on consecutive days in October, 1985. Those contaminants that occurred above 1 µg/L for more than 50% of the time in the final effluent are shown in Table 5. Data for these contaminants should be regarded as preliminary because the project is still in progress.

The Little River and Belle River STPs are secondary plants. A high quality nitrified effluent was produced at Little River and a partially

TABLE 4 CONCENTRATION OF MOST FREQUENTLY FOUND TRACE CONTAMINANTS IN THE EC/MOE VARIABILITY STUDY EFFLUENTS(12)

CONTAMINANT (μg/L)	WATERLOO		WELLAND		GALT	
	Inf.	Eff.[1]	Inf.	Eff.[1]	Inf.	Eff.[1]
Volatiles						
Chloroform[2]	5.2	**1.0**	5.1	**L**	3.3	**1.0**
1,4-Dichlorobenzene	2.9	**L**	2.2	**L**	4.2	**1.4**
Tetrachloroethylene[2]	ND[3]	**ND**	ND	**ND**	27.7	**8.6**
1,1,1-Trichloroethane[2]	1.4	**L**	ND	**ND**	5.2	**2.2**
Trichloroethylene	1.7	**L**	1.3	**L**	4.4	**1.0**
p-& m-Xylene	50.4	**L**	1.2	**L**	39.6	**1.0**
Metals						
Cadmium	4.5	**4.3**	2.9	**2.6**	6.2	**2.4**
Chromium[2]	54.2	**29.8**	16.5	**9.3**	92.8	**31.0**
Copper[2]	122	**14.3**	34.1	**6.3**	146	**49.2**
Nickel[2]	27.3	**24.7**	15.1	**13.3**	111	**66.6**
Lead	20.4	**6.7**	12.2	**5.6**	13.9	**5.4**
Zinc[2]	152	**81.4**	76.2	**22.9**	199	**83.2**
Conventionals (mg/L)						
FOC	48.0	**13.2**	28.0	**8.2**	51.0	**16.5**
TSS	137	**5.8**	73.9	**3.8**	102	**34.2**

---

[1] Mean values for those contaminants present in treated effluents with mean concentrations greater than 1.0 μg/L. Other values designated L indicate that the contaminant occurred less than 50% of the time. Corresponding influent concentrations are mean values.

[2] In the list of the most frequently found effluent contaminants of both 25 and 40 POTW Studies.

[3] ND - Not detected.

TABLE 5 CONCENTRATION OF MOST FREQUENTLY FOUND TRACE CONTAMINANTS IN THE UGLCCS STP EFFLUENTS(13)

CONTAMINANT (μg/L)	LITTLE RIVER		BELLE RIVER		WINDSOR WESTERLY	
	Inf.	Eff.[1]	Inf.	Eff.[1]	Inf.	Eff.[1]
Volatiles						
Bromodichloromethane	0.5	**L**	0.3	**5.8**	1.4	**1.4**
Chloroform[2] [3]	5.0	**17.6**	4.6	**7.3**	6.0	**6.4**
Dibromochloromethane	ND[4]	**L**	ND	**2.3**	ND	**L**
Ethyl benzene	0.2	**ND**	<0.1	**ND**	5.5	**9.6**
Methylene chloride[2]	2.8	**L**	2.3	**L**	11.9	**12.5**
Tetrachloroethylene[2] [3]	0.7	**L**	<0.1	**L**	36.4	**69.0**
1,1,1-Trichloroethane[2] [3]	0.4	**ND**	ND	**ND**	2.5	**2.0**
Toluene[2]	3.2	**3.4**	0.7	**L**	17.4	**21.0**
p-& m-Xylene[3]	0.7	**ND**	0.2	**L**	83.5	**40.4**
o-Xylene	0.4	**ND**	0.1	**L**	11.4	**17.0**
Base Neutrals						
1,2-Dichlorobenzene	0.5	**ND**	1.7	**L**	1.5	**1.9**
1,4-Dichlorobenzene	1.5	**L**	1.0	**L**	1.8	**1.5**
Bis(2-EH)phthalate[2]	17.3	**5.3**	10.7	**79.3**	25.3	**12.8**
Butyl benzyl phthalate	5.5	**L**	2.3	**L**	4.3	**7.7**
Di-n-butyl phthalate[2]	55.0	**47.8**	11.3	**16.7**	58.3	**22.0**
Diethyl phthalate	13.0	**L**	10.6	**L**	8.2	**4.8**
Di-n-octyl phthalate	21.0	**16.7**	17.6	**27.7**	16.3	**21.7**
Metals						
Chromium[2] [3]	32	**8**	20	**L**	56	**10**
Copper[2] [3]	41	**18**	40	**10**	46	**22**
Nickel[2]	19	**10**	20	**L**	39	**37**
Zinc[2] [3]	196	**73**	50	**36**	329	**125**
Conventionals (mg/L)						
BOD5	95	**4**	63	**3**	84	**32**
TSS	96	**13**	44	**3**	104	**12**
NH_3 N	12	**0.4**	12	**2.7**	7	**6**

---

[1] Mean values for those contaminants present in treated effluents with mean concentrations greater than 1.0 μg/L. Other values designated L indicate that the contaminant occurred less than 50% of the time. Corresponding influent concentrations are mean values.

[2] In the list of the most commonly found effluent contaminants in both 25 and 40 POTW Studies.

[3] In the list of the most frequently found effluent contaminants in both the Niagara Region and the EC/MOE Variability Studies.

[4] ND - Not detected.

nitrified effluent at Belle River. Windsor Westerly STP is a primary plant that also produced a good quality effluent. As was observed in the comparison between the Niagara Region STPs (Table 3), there is a greater pass through of organic contaminants at the primary plant when compared to the secondary plants. The level of pass through appears to be greater at the Windsor Westerly STP than either Fort Erie or Niagara Falls STPs in terms of the volatile contaminants. All three STPs recorded the presence of phthalate esters which were not analyzed for in the Niagara Region Study. Of the seven organic contaminants listed in Table 5 for Little River and Belle River, four were in the list of the most frequently occurring contaminants in the 25 and 40 POTW Studies. For Windsor Westerly, however, seventeen organic contaminants are listed in Table 5 of which seven were in the 25 and 40 POTW list. Metal contaminants were prevalent in all three STP effluents similar to the observation at Niagara Region. There are inadequate data to demonstrate whether there is a significant difference in metals remaining in the effluent after primary versus secondary treatment.

U.S. Facilities

No large survey has been carried out in the U.S. since the completion of the 25 and 40 POTW Studies, probably as a result of the high cost. The literature shows that only some of the large U.S. municipalities have undertaken limited surveys of trace contaminant removal in STPs.

A one year investigation, called the Toxicant Pretreatment Planning Study (TPPS), was conducted by the Municipality of Metropolitan Seattle of Metro's two STPs(14). Seventeen 24 hr flow composited samples of influents and effluents were collected during the period 1980 to 1981. Those contaminants that occurred above 1 μg/L for more than 50% of the time in the final effluent are shown in Table 6. The Renton plant is a secondary plant which produced a high quality effluent during the Study as defined by the conventional parameters. Nine organic contaminants are listed in Table 6 of which five are from the 25 and 40 POTW list (Table 1). West Point is a primary plant and demonstrated a greater pass through of contaminants than Renton. Thirteen frequently occurring organic contaminants were identified; nine were the same as those at Renton and were

TABLE 6 - CONCENTRATION OF MOST FREQUENTLY FOUND TRACE CONTAMINANTS IN THE TPPS STP EFFLUENTS(14)

CONTAMINANT (µg/L)	RENTON		WEST POINT	
	Inf.	Eff.[1]	Inf.	Eff.[1]
Volatiles				
Benzene	2.6	**2.8**	3.1	**3.8**
Chloroform[2]	2.9	**2.8**	9.1	**7.4**
Ethyl benzene	1.8	**L**	8.1	**10.4**
Methylene chloride[2]	37.1	**29.2**	45.3	**57.1**
Tetrachloroethylene[2]	20.0	**3.9**	14.7	**18.7**
Trichloroethylene	22.2	**2.6**	11.7	**8.3**
Toluene[2]	9.5	**L**	47.0	**51.2**
Base Neutrals				
Naphthalene	ND[3]	**ND**	12.7	**10.4**
Butyl benzyl phthalate	56.8	**19.0**	57.3	**48.5**
Diethyl phthalate	8.9	**1.7**	4.2	**5.3**
Di-n-butyl phthalate[2]	48.6	**32.8**	40.3	**38.8**
Di-octyl phthalate	49.2	**10.8**	21.7	**60.1**
Acid Extractables				
Phenol	67.6	**L**	46.7	**42.5**
Metals				
Antimony	1.4	**2**	5.5	**7**
Arsenic	4.9	**2**	3.8	**4**
Cadmium	7.8	**1**	7.2	**4**
Chromium[2]	86	**33**	120	**64**
Copper[2]	200	**29**	180	**88**
Lead	120	**25**	160	**74**
Nickel[2]	57	**31**	64	**51**
Silver	13	**3**	13	**8**
Zinc[2]	240	**64**	340	**140**
Inorganics				
Cyanide[2]	26	**27**	47	**59**
Conventionals (mg/L)				
BOD5	242	**20**	207	**132**
TSS	211	**20**	215	**104**

---

[1] Mean values for those contaminants present in treated effluents with mean concentrations greater than 1.0 µg/L. Other values designated L indicate that the contaminant occurred less than 50% of the time. Corresponding influent concentrations are mean values.

[2] In the list of most frequently found effluent contaminants in both 25- and 40 POTW Studies.

[3] ND - Not detected.

present at higher concentrations. Nine metal contaminants were identified as occurring frequently at both plants; four were on the 25 and 40 POTW lists.

The Ohio and Wisconsin State Environmental Protection Agencies and the Metropolitan Sanitary District of Greater Chicago (MSDGC), have conducted limited organic analysis of STP effluents during the period 1983 to 1984(cited by 8). The most frequently found contaminants were very similar at all locations. Common to the surveys were the following six contaminants:

Volatiles	Base Neutrals
Chloroform	Bis(2-EH)phthalate
Methylene chloride	Di-n-octyl phthalate
1,1,1-Trichloroethane	
Trichloroethylene	

Four of these were on the list of most frequently found contaminants in the 25- and 40 POTW Studies (Table 1). The Wisconsin EPA (WEPA) and the MSDGC listed six additional frequently occurring contaminants:

Volatiles	Base Neutrals
Benzene (WEPA only)	1,4-Dichlorobenzene (WEPA only)
Tetrachloroethylene	Diethyl phthalate
Toluene (WEPA only)	Di-n-butyl phthalate (WEPA only)

These contaminants were also frequently found in the studies cited above.

Discussion of Survey Results

Trace contaminant data were screened from 105 municipal treatment plant effluents in Canada and the U.S.. The period over which these data were collected ranged from 1978 to 1986. The contaminants listed below were found most frequently in STP effluents. Cyanide was also found when tested for.

Volatiles

- Chloroform
- Methylene chloride
- Tetrachloroethylene
- Toluene
- 1,1,1-Trichloroethane
- p-& m-Xylene

Phthalates

- Bis(2-ethyl hexyl)phthalate
- Di-n-butyl phthalate
- Diethyl phthalate

Metals

- Cadmium
- Chromium
- Copper
- Lead
- Nickel
- Zinc

The chlorinated solvent compounds, chloroform, methylene chloride, tetrachloroethylene and trichloroethane were found most frequently, and, to a lesser extent, the solvents toluene, ethyl benzene and the chlorinated benzenes were also found. More recent surveys have identified the frequent presence of xylenes. In well operated secondary plants, the level of the most commonly found volatiles ranged from 1 to 20 µg/L. For methylene chloride and other chlorinated compounds the higher effluent values may be distorted. Methylene chloride is used as the extracting solvent in the analytical protocol for USEPA priority pollutants. It can occur as a contaminant in laboratory glassware. Also, chlorination of treated effluents can increase the level of purgeable organics in final effluents over that found in raw wastewaters. Where chlorination does not occur, purgeable compounds are usually removed to a high degree but may still be present above detectable levels. In primary STPs, the same types of purgeable compounds were observed. Their concentration may be higher than in secondary STP effluents.

Not all effluents were measured for phthalates. However when this was carried out, all effluent samples contained phthalate esters. Their widespread use in plasticizers leads to their ubiquitous presence in all wastewater samples. They are among the most commonly occurring organic contaminants in treated effluents. Metal contaminants occurred at greater concentrations than the organic contaminants, ranging from 1 to 100 µg/L in secondary effluents and often higher in primary effluents.

The absence of phenolic compounds in treated effluents may be attributed to biological oxidation. However, this may not be appropriate for primary plants. The method of measuring phenol is not frequently reported. The extraction efficiency of phenol by methylene chloride can be low depending upon organic matrix effects. Therefore, artificially low values can be reported. This phenomenon may be avoided by measuring phenol by the 4-amino antipyrene method.

The effectiveness of secondary treatment plants can be demonstrated by comparing influent and effluent data. In many cases, contaminants occur less than 50% of the time in treated effluents despite their relatively high influent values.

There has been concern over the presence of PAHs in effluent discharges. The EC/MOE Variability Study measured 100 samples of influent and effluent at two hour intervals over eight days at three different STPs. Despite this rigorous investigation, PAHs were rarely, if ever, detected in either influents or effluents.

In summary, well operated secondary STPs can produce high quality effluents that contain small numbers of frequently occurring priority pollutants. Typically, between five and ten organic contaminants were found at concentrations ranging from 1 to 20 µg/L more than 50% of the time. The significance of the ubiquitous presence of methylene chloride and the phthalate esters in all effluent samples is not understood at this time. In addition, between three and six metal contaminants were found more than 50% of the time at concentrations ranging from 1 to 100 µg/L.

TECHNOLOGY OF CONTAMINANT REMOVAL

It may be possible to further improve the effluent quality that is being achieved at the present time by a better understanding of contaminant removal mechanisms. A review of the current knowledge on removal mechanisms follows.

In parallel with STP performance assessments, considerable work has been carried out since 1978 to improve the understanding regarding toxic contaminant removal in wastewater treatment plants. Most work has addressed the activated sludge system with very little work directed to primary or other secondary plants. What has emerged is the knowledge that the mechanism(s) of removal are complex and do not lend themselves readily to predictive models. It has been established that organic contaminants can be removed in secondary plants by adsorption, volatilization and by biological oxidation. Metal contaminants may be removed by either precipitation or adsorption. If removal does not occur by one of these mechanisms, the contaminants pass through to the final effluent and are discharged.

Several attempts(15,16,17) have been made to mathematically model the contaminant removal mechanisms. Of these attempts, the volatilization and biosorption models are better developed than the biodegradation model. It is likely that a limited number of microbial species may be responsible for biodegradation of a specific contaminant. However, since isolation of the microorganisms or enzymes is almost impossible, no adequate mechanistic model has been developed. The predictive equations are derived from steady-state conditions which are not representative of the typical operation of an STP. The existing models cannot address dynamic behaviour. They have not been field tested because of this drawback.

Early work by the USEPA assessed the removal of trace contaminants in well operated and acclimated pilot-scale activated sludge systems(10,18,19). Process performance was evaluated using controlled influent concentrations of priority pollutants in municipal wastewaters. Typical spiked concentrations of the contaminants ranged from 50 to 200 µg/L. More than 95% removal of acid extractable and base neutral contaminants was achieved, with more than 98%

removal for the volatiles. Trace metal removals were lower, ranging from 20 to 90%. An important observation was, that at the levels of contaminant tested, inhibitory or interference effects were not observed on the biological treatment system when operated at steady-state.

Treatability investigations sponsored by the USEPA(16,20) suggested that the abiotic removal mechanisms could dominate biological oxidation. Contaminants could partition to sludges which could prevent land disposal of such sludges. Alternatively, they could volatilize into the air from sewers, headworks and aeration basins. The contribution of the three mechanisms to removal has been estimated by many researchers. Unfortunately, removal has not always been attributed to the correct mechanism(8). Consequently, direct comparison of removals attributed to specific mechanisms is not always possible.

The experimental work of Weber and Jones(16), Kirsch et al.(20), Kincannon et al.(21) and Lawson and Siegrist(22) indicated that volatilization and biodegradation were the major removal mechanisms, with adsorption being less important. The USEPA addressed the relative importance of the removal mechanisms through non-experimental procedures(23). In this procedure, the USEPA first established the removal of a compound and then estimated the proportion of the contaminant removed by volatilization based on USEPA data. The proportion of the compound that was adsorbed to the biomass was estimated from the 40 POTW Study data(1) while the proportion biodegraded was calculated by the difference. The procedure is useful in that it differentiates between acclimated and unacclimated systems. The procedure indicated that volatile contaminants are removed primarily by volatilization, or biodegradation, depending upon the degree of acclimation of the activated sludge. Volatilization may be the dominant mechanism when the activated sludge system is not acclimated. Conversely, if the biomass is acclimated, biodegradation may be the important mechanism. This effect has been demonstrated by Bedford and Melcer(24) for trichloroethylene. In the base neutral group, the chlorinated benzenes are removed by volatilization and biodegradation. With the non-experimental approach, adsorption was assigned a greater role than in previous studies. The phthalate esters were predicted to be removed by a combination of biodegradation and adsorption. PAHs appear to be degraded and adsorbed. Phenolic compounds appear to be biodegraded primarily.

CONTROL TECHNOLOGY

Trace contaminants may be removed by volatilization, adsorption or biological oxidation. In view of the potential problems associated with the loss of contaminants by the first two mechanisms, a reduction in effluent emissions could best benefit from an improvement in the biological oxidation mechanism. Substrate inhibition and microbial growth rate are important process considerations in the biological degradation of trace contaminants. To minimize substrate inhibition, measures could be taken to reduce the influent contaminant concentration by minimizing the input of the contaminants to the sewer. This is a matter which is beyond the scope of this paper.

Microorganisms that can degrade complex organic contaminants have low growth rates. The inverse relationship between the specific microbial growth rate and SRT permits the control of growth rate through SRT manipulation. To prevent the washout of slow-growing microorganisms, a minimum SRT must be maintained such that microbial growth can proceed at, or less than, its maximum rate. Wash-out will then be prevented. To minimize construction costs, it is desirable that HRT and SRT be adjustable independently. In fixed film systems, such as rotating disc contactors and biological fluidized beds, this can be achieved readily. In activated sludge systems, SRT may be manipulated by adjustment of sludge recycle rate and sludge wasting.

Several researchers (25-28) have demonstrated the importance of SRT manipulation for removal of trace contaminants in activated sludge systems. The latter two studies showed that a minimum SRT of five days was required for the removal of 4,6-dinitro-o-cresol from municipal sewage and ten days for the removal of pentachlorophenol, also from municipal sewage. Lower SRTs resulted in pass through of the contaminant and a deterioration in settling performance.

CONCLUSIONS

- A survey of treated effluents from 105 municipal wastewater treatment plants indicated that very low levels of USEPA priority pollutants can be achieved in the effluents from well operated secondary plants despite the often high levels that occurred in raw wastewaters. A greater pass through of both organic and inorganic contaminants occurred in primary plants.

- The most commonly occurring contaminants from the volatile, acid extractable, base-neutral and metal groups of the priority pollutants, were the volatile chlorinated compounds, phthalate esters and metals. PAHs were not frequently found.
- Typically, for well operated secondary STPs, between five and ten organic contaminants were found at concentrations ranging from 1 to 20 µg/L more than 50% of the time in the effluents. Between three and six metal contaminants were found more than 50% of the time, ranging in concentrations from 1 to 100 µg/L.
- Trace contaminants are removed in municipal wastewater treatment systems via volatilization, adsorption and biodegradation mechanisms. The contribution made by each mechanism for a specific contaminant is not well known or understood. Modelling of the removal mechanisms is at an early stage.
- The concept of SRT manipulation has been demonstrated to achieve control of trace contaminants in municipal activated sludge systems.

REFERENCES

1. Burns and Roe Industrial Services Corporation, "Fate of Priority Toxic Pollutants in Publicly Owned Treatment Works - Final Report", Vol.1, EPA-440/1-82/303, 1982.

2. Hannah, S.A. and L.A. Rossman, "Monitoring and Analysis of Hazardous Organics in Municipal Wastewater - A Study of 25 Treatment Plants". NTIS Pub.No. PB83-155713, 1982.

3. Bonner, R.F. and O. Meresz, "St. Clair River Organics Study - Identification and Quantitation of Organic Compounds". Ontario Ministry of Environment, Toronto, Ont., 1981.

4. Water Pollution Control Directorate, "Draft Summary Report: Toxic Screening Studies at Municipal Sewage Treatment Plants 1979-1981". Abatement and Compliance Branch, Municipal Division, Environment Canada, Ottawa, Ont., 1982.

5. Rossman, L.A. and J.J. Convery, "A Perspective on Performance Variability in Municipal Wastewater Treatment Facilities", NTIS Pub.No. PB86-176377, 1986.

6. Bridle, T.R. et al., "Biological Treatment of Coke Plant Wastewaters For Control of Nitrogen and Trace Organics". Presented at the 53rd Annual Water Pollution Control Federation Conference, Las Vegas, 1980.

7. Mann Testing Laboratories, "Trace Organic Analysis of WPC Plant Influent and Effluent". Report to the Municipality of Metropolitan Toronto, Metro Works Department, Toronto, Ont., 1986.

8. Canviro Consultants Ltd., "A Novel Application of a Time Series Modelling Approach to the Management of Dynamic Fluctuations in Trace Contaminants in Sewage Treatment Plants" - Phase 1 Report: Technical Review. Wastewater Technology Centre, Environment Canada, Burlington, Ont., 1986.

9. Hannah, S.A., et al., "Comparative Removal of Toxic Pollutants by Six Wastewater Treatment Processes", J.Wat. Pollut. Contr. Fed., 58(1), 27, 1986.

10. Petrasek, A.C. and I.J. Kugelman, "Metals Removals and Partitioning in Conventional Wastewater Treatment Plants", J. Wat. Pollut. Contr. Fed., 55(9), 1183, 1983.

11. Canviro Consultants Ltd., "Removal of Hazardous Contaminants in the Hamilton WPCP". Draft Report submitted to Ontario Ministry of Environment, Toronto, Ont., 1984.

12. Canviro Consultants Ltd. Preliminary Data from the Study on the Management of Dynamic Fluctuations in Trace Contaminants in Sewage Treatment Plants. Wastewater Technology Centre, Environment Canada, Burlington, Ont., 1986.

13. Environment Canada. Preliminary Data from Great Lakes Inter-Connecting Channel Study. Toronto, Ont., 1986.

14. Cooley, R. and R. Matasci, "Toxicant Pretreatment Study Technical Report A1-Treatment Plant Evaluation". Report to Municipality of Metropolitan Seattle, WPC Department., Seattle, WA., 1984.

15. Blackburn, J.W. et al., "Organic Chemical Fate Prediction in Activated Sludge Treatment Processes". NTIS Report No. PB85-247674, 1985.

16. Weber, W.J. and B.E. Jones, "Toxic Substance Removal in Activated Sludge and PAC Treatment Systems". NTIS Report No PB86-182425, 1986.

17. Moos, L.P. et al., "Pentachlorophenol Biodegradation - I (Aerobic)", Wat. Res., 17, 1575, 1983.

18. Petrasek, A.C. et al., "Fate of Toxic Organic Compounds in Wastewater Treatment Plants", J. Wat. Pollut. Contr. Fed., 55(10), 1286, 1983.

19. Petrasek, A.C. et al., "Removal and Partitioning of Volatile Organic Priority Pollutants in Wastewater Treatment Plants". Proc. of 9th U.S.-Japan Conf. on Sewage Treatment Technology, EPA-600/9-85/014, 1985.

20. Kirsch, E.J. et al.. "Fate of Eight Organic Priority Pollutants", Draft Report, EPA Cooperative Agreement No. CR-807630-10, WERL, USEPA, Cincinnati, 1986.

21. Kincannon, D.F. et al., "Removal Mechanisms for Toxic Priority Pollutants", J. Wat. Pollut. Contr. Fed., 55, 157, 1983.

22. Lawson, C.T. and S.A. Siegrist, "Removal Mechanisms for Selected Priority Pollutants in Activated Sludge Systems", Proc. of ASCE Nat. Conf. on Environ. Eng., 356, 1981.

23. U.S. Environmental Protection Agency, "Report to Congress on the Discharge of Hazardous Wastes to Publicly Owned Treatment Works. EPA/530-SW-86-004, 1986.

24. Bedford, W.K. and H. Melcer, "Fate of Trichloroethylene in Activated Sludge Systems". Presented at 21st Canadian Symposium on Water Pollution Research, Burlington, Ontario, 1986.

25. Wukasch, R.F. et al., "Prediction of the Fate of Organic Compounds in Biological Wastewater Treatment Systems". AIChE Symposium Series (Water 1980), No. 209, 137, 1981.

26. Bridle, T.R. et al., "Biological Nitrogen Control of Coke Plant Wastewaters", Wat.Sci.Tech., 13(1), 667, 1981.

27. Melcer, H. and W.K. Bedford, "The Fate of 4,6-Dinitro-o-cresol in Municipal Activated Sludge Systems". Presented at the International Conference on Innovative Biological Treatment of Toxic Wastewaters, Arlington, VA, 1986.

28. Melcer, H. and W.K. Bedford, "Removal of Pentachlorophenol in Municipal Activated Sludge Systems". Presented at the 59th Annual Water Pollution Control Federation Conference, Los Angeles, 1986.

DESIGN OF PILOT PROGRAM FOR ORGANICS REMOVAL AT NIAGARA FALLS

J.N. Hilton*, R.F. Machacek*, M.C. Kavanaugh** and K.J. Roberts***

*MacLaren Plansearch Inc., 33 Yonge Street, Toronto, Ontario, Canada M5E 1E7
**James M. Montgomery, Consulting Engineers Inc., 250 N. Madison Avenue,
Pasadena, California, U.S.A. 91109
***Ontario Ministry of the Environment, 1 St. Clair Ave. West,
Toronto, Ontario, Canada M4V 1K6

ABSTRACT

As public concern for the quality of drinking water in Ontario continues to grow, considerable research has been undertaken to re-examine conventional treatment methodologies as well as alternate processes for the removal of trace levels of organic chemicals, including adsorption by granular activated carbon (GAC).

This project has been undertaken to determine the following:

- the effectiveness of optimized conventional drinking water treatment for the removal of trace organic contaminants
- the effectiveness of activated carbon adsorption removals of trace organic contaminants when used in the add-on contactor mode
- process operational parameters for the optimized operation of full scale water treatment plants and GAC adsorbers used in the add-on mode for organics removal.

Jar testing and pilot plant operations will be conducted on site at the Niagara Falls Water Treatment Plant, using the Niagara River as the raw water source.

This paper summarizes work performed thus far on the selection of target monitoring compounds, the development of analytical protocols, the proposed experimental plan (including jar testing, conventional treatment, GAC treatment), the design of the pilot plant, and the analysis of data.

KEYWORDS

Trace organics removal; drinking water treatment; adsorption; granular activated carbon; homogeneous surface diffusion model; equilibrium column model.

INTRODUCTION

Public concern for the quality of drinking water in Ontario continues to grow, as advances in analytical capabilities result in the detection of an increasing number of synthetic organic compounds (SOC) in raw waters. This awareness has been heightened by widespread publicity from the news media of the presence of even the smallest concentrations of organics in raw and finished drinking water supplies.

As a result, considerable research is being undertaken to re-examine conventional treatment methodologies as well as alternate processes for the removal of trace levels of organic chemicals, including adsorption by granular activated carbon (GAC).

This project has been undertaken to determine the following:

- the effectiveness of optimized conventional drinking water treatment for the removal of trace organic contaminants
- the effectiveness of activated carbon adsorption removals of trace organic contaminants when used in the add-on contactor mode
- process operational parameters for the optimized operation of full scale water treatment plants and GAC adsorbers used in the add-on mode for organics removal.

The project comprises three components. The first component includes a review of existing data on ambient water quality, development of analytical and sampling protocols, experimental design development and the physical design and set-up of the pilot plant equipment. Component II consists of organic removal studies at Niagara Falls, Ontario, including jar testing and pilot plant operation. Jar testing will determine an initial choice of coagulant for conventional treatment and will be re-evaluated throughout the year. The pilot plant will model a complete water treatment process and will operate to optimize organics removal conventional processes for a period of two weeks. The pilot plant will then operate with GAC fixed beds in the add-on contactor mode for a period of 52 weeks. The third component consists of data evaluation including results of GAC modelling runs. The ultimate goal is to generate data that will be of a nature to develop pertinent design criteria and serve as a technical basis for policy regarding drinking water quality and required treatment in Ontario.

At this time, work on Component I is nearing completion. This paper summarizes work performed thus far on the selection of target monitoring compounds, the development of analytical protocols, the proposed experimental plan (including jar testing, conventional treatment, GAC treatment), the design of the pilot plant, and the analysis of data.

SELECTION OF TARGET COMPOUNDS

The initial selection process for target compounds to be monitored during the pilot plant operation began with a list of over 300 organic chemicals that have been found in the Great Lakes ecosystem. This list was compiled from several different references, including work by the International Joint Commission (IJC, 1983), the Niagara River Toxics Committee (NRTC, 1984), the Ontario Ministry of the Environment (MOE, 1984, 1985a, 1985b), the New York Public Interest Group (NYPIRG, 1981), the City of Toronto Department of Public Health (City of Toronto, 1984) and the Municipality of Metropolitan Toronto Department of Works (Municipality of Metro Toronto, 1983).

The following information was gathered for each chemical:

Identification

Chemical Name

CAS - Chemical Abstracts Service Registry Number

Environmental Levels

The frequency and maximum amount detected in the Niagara Falls water treatment plant raw water by routine, bi-weekly MOE monitoring of organics.

Physical, Chemical and Toxicological Properties

Henry's Law Constant
Aqueous Solubility
log Kow
Complexation Potential with TOC
Liquid Phase Diffusion Coefficient
Activated Carbon Capacity
Bioconcentration Factor
LC50
LD50
NRTC Hazard Class Rating

Aquatic and Drinking Water Criteria

Ministry of the Environment
U.S. Environmental Protection Agency
World Health Organization

The initial screen of all the chemicals found in the Great Lakes ecosystem was based on the availability of quantitative environmental and toxicological data. Compounds without much data available were given little further consideration. The second screen for chemicals with quantitative data was based mainly on the Categories of Concern developed by the Niagara River Toxics Committee (NRTC, 1984). One of the principal tasks of the NRTC was to assess the significance of the types and levels of chemicals found in the Niagara River. The screening methodology involved in establishing a priority ranking involved three major types of information. Criteria information was taken from several agencies and included criteria for the protection of aquatic life, human health, etc. Chemical and toxicological information included bioaccumulation and accute toxicity data, and other health parameters considered in various other toxicity scoring methodologies. Environmental occurrence information was compiled from responsible jurisdictions involved in the Niagara River Toxics Project. The screening process resulted in three major groups and several subgroups of chemicals, of which group I, and groups IIA and IIB chemicals are considered to be of most concern. This is based on concentrations of these chemicals identified in the Niagara River with respect to levels at which they are considered to pose risks to human health and/or environment. Designation as an EPA priority pollutant was also considered in the screening process.

For this project, chemicals listed as NRTC group I, IIA or IIB compounds or as EPA priority pollutants were screened again to determine if they were present in the raw water supply at the Niagara Falls Water Treatment Plant. This was accomplished by reviewing MOE routine, biweekly monitoring of several classes of organic compounds in the Niagara raw water over a period of two years. This was done to help establish sampling and spiking needs in the overall experimental plan.

Compounds not passing previous screens were then considered against other compounds in the same chemical class (e.g. pesticides, phthalates, polyaromatic hydrocarbons). An attempt was made to have a complete range of high to low values of chemical and physical properties that affect organic chemical removal processes represented within each chemical class. For example, Henry's Law Constants provide an indication of the ability of a chemical to be removed by aeration or air stripping processes. Compounds that were felt to contribute to the overall range of properties within their class were considered further.

The final acceptance criteria was based on practical considerations for the spiking, sampling and analytical programs. Chemicals that presented problems were rejected. For example, compounds for which acceptability low detection limits could not be achieved were excluded. Another example is the phthalates (i.e. bis(2-ethylhexyl) phthalate and di-n-butylphthalate) which are ubiquitous as laboratory contaminants.

The total number of target compounds is limited by budget constraints, as analytical costs for regular monitoring of 34 organic compounds are quite large. The list of target compounds chosen is shown in Table 1.

TABLE 1 List of Target Compounds

Chemical Class	Compounds
Halogenated Aliphatics	Chloroform Carbon tetrachloride 1,2-dichloroethane Hexachlorobutadiene Tetrachloroethylene
Aromatics	Benzene o-Xylene Nitrobenzene
Chlorinated Benzenes	Chlorobenzene 1,4-dichlorobenzene Hexachlorobenzene 1,2,4-trichlorobenzene
Chlorinated Phenols	2,4,6-trichlorophenol Pentachlorophenol
PCB's	2,5,2'-trichlorobiphenyl 2,5,2',5'-tetrachlorobiphenyl 2,4,5,2',5'-pentachlorobiphenyl 2,4,5,2'4',5'-hexachlorobiphenyl 2,3,4,5,2',3',4',5'-octachlorobiphenyl
Organochlorine Pesticides	p,p'-DDT Heptachlor epoxide beta-BHC
Chlorophenoxy Herbicides	2,4-D
PAH's and Related Compounds	Anthracene Benzo(a)pyrene Naphthalene Pyrene

Phthalates	Di-n-octylphthalate
Alcohols and Esters	1-decanol Isobutanol Methyl hexadecanoate
Alkanes	Decane Hexadecane Hexane

ANALYTICAL PROTOCOL DEVELOPMENT

The 34 compounds selected for this project have been divided into five analytical fractions based on their chemical properties. These five analytical fractions and the compounds belonging in each category are summarized below.

High Volume Volatile Organic Analysis

An optimization of the classic purge-and-trap analysis wherein 100 mLs of water are purged with helium onto an adsorbent trap and desorbed into a capillary column with GCMS detection.

- chloroform
- carbon tetrachloride
- 1,2-dichloroethane
- tetrachloroethane
- benzene
- xylene
- chlorobenzene
- 1,4-dichlorobenzene
- 1,2,4-trichlorobenzene
- isobutanol
- hexane
- decane
- naphthalene

High Volume Base/Neutral Analysis

A modification of the liquid-liquid extraction procedure wherein a 16 liter sample is extracted serially with methylene chloride at high pH and the final extract analysed by GCMS.

- nitrobenzene
- di-n-octylphthalate
- 1-decanol
- methyl
- hexadecanoate
- hexadecane

High Volume Oganochlorine Pesticides Analysis

A modification of the liquid-liquid extraction procedure wherein a 16 liter sample is extracted serially with methylene chloride, the solvent switched to hexane and the final extract analysed by GC/ECD.

hexachlorobenzene
hexachlorobutadiene
beta-BHC
p,p'-DDT
heptachlor epoxide
2,5,2'-trichlorobiphenyl
2,5,2',5'-tetrachlorobiphenyl
2,4,5,2',5'-pentachlorobiphenyl
2,4,5,2',4',5'-hexachlorobiphenyl
2,3,4,5,2',3',4',5'-octachlorobiphenyl

High Volume Polyaromatic Hydrocarbons Analysis

A modification of the liquid-liquid extraction procedure wherein a 16 liter sample is extracted serially with methylene chloride, the solvent switched to acetonitrile and the final extract analysed by HPLC with UV and fluorescence detectors.

anthracene
benzo (a) pyrene
pyrene
naphthalene

High Volume Chlorinated Phenol/Chlorophenoxy Herbicide Analysis

A modification of the liquid-liquid extraction procedure wherein a 16 liter sample is adjusted to low pH and serially extracted with methylene chloride, the solvent transferred to toluene, derivitized with a boron trifluoride reagent, and analysed by GC/ECD.

2,4,6-trichlorophenol
pentachlorophenol
2,4-D

Precision and Accuracy

Detection limits for the analytical methods used in this project have not yet been finalized. The method detection limit (MDL) will be used in the reporting of all results from organics analysis.

The MDL measures the minimum concentration of analyte required to yield a signal which is distinguishable from the signal due to the blank, and is generally much higher than the more typically reported instrument detection limit, which is based on a simple signal to noise response. The MDL is actually a function of method precision at low concentration levels, since the ability to distinguish a true signal from the blank is dependent on the variability of a replicate measurements for the blank and for low level samples. The MDL is, therefore, dependent on the standard deviation of replicate blank and low level sample replicates.

The MDL is based on hypothesis testing using the student's t statistic on the population of data obtained by replicate testing. The statistical values for a 99% confidence level have been applied to work on this project.The estimated MDL is calculated by multiplying the t statistic for 99% confidence and the appropriate degrees of freedom (dependent on number of replicates) by the standard deviation value measured for the replicates. Precision is reported as the relative standard deviation of replicate measurements of samples spiked with a known concentration of analyte. Accuracy is reported as the percent recovery of the mean of replicate measurements of samples spiked with a known concentration of analyte.

EXPERIMENTAL PLAN

Jar Testing Studies

The goal of the jar testing studies is to determine the optimum coagulant dose and operating pH for removal of turbidity and natural organic carbon. As a measure of natural organic carbon, dissolved organic carbon (DOC) and UV absorbance will be used. The optimum conditions will be selected through bench-scale testing at the beginning of pilot plant operation, and quarterly thereafter to adjust for seasonal water quality variations.

The jar tests will be used to screen a large number of potential coagulants, coagulant doses, and operating pH combinations. In general, optimum turbidity removal occurs at a higher pH than optimum DOC removal at a given coagulant dose. Thus, selection of a coagulant dose/pH combination represents a compromise between turbidity removal and DOC removal. Three factors must be integrated to determine the optimum dose: removal efficiency, sludge production and cost.

The coagulation optimization consists of a series of steps to evaluate a large number of options. The first step is to characterize the water quality with respect to the level of natural organics, turbidity, pH, alkalinity and buffer capacity. Step 2 is to evaluate the following primary coagulants: alum, polyaluminum chloride, ferric chloride, and CatFloc with alum (at a fixed alum dose). These tests will be done at a fixed pH. Following coagulation selection, step 3 tests would investigate the dose/pH relationship. The treated water quality will be used to generate DOC and turbidity isopleths as a function of pH and coagulant dose. The minimum coagulant dose giving DOC and turbidity removals will be compared, based on estimated costs of chemical addition and sludge disposal. Sludge production will be estimated from stoichiometry. The objective of step 4 is to determine the benefits of anionic, nonionic and long-chain cationic polymers as well as activated silica as secondary coagulants for improving DOC and/or turbidity removals.

Monthly average raw water turbidity at Niagara Falls varies from approximately 0.6 to 14 NTU throughout the year. Thus, the coagulant dose will also vary. Quarterly (or more frequent) jar test series will thus be conducted to determine coagulant dose, pH and polymer dose with changing raw water quality.

Evaluation of Organics Removal by Conventional Treatment

Goal. The goal of this phase of the study is to determine the effectiveness of conventional water treatment unit processes (e.g. coagulation, flocculation, sedimentation and filtration) in removing the target compounds.

Compound selection. Based on the selection of the 34 target compounds from among eleven groups of SOCs, fourteen "monitor" compounds were selected for this phase of the study. These compounds were selected to represent a wide range of physiochemical characteristics relevant to water treatment processes. These monitor compounds are:

- 1,2-Dichloroethane
- Tetrachloroethylene
- Benzene
- Chlorobenzene
- 1,4-Dichlorobenzene
- 2,4,6-Trichlorophenol
- PCB congeners
- p,p'-DDT
- beta-BHC (alpha-BHC)
- Anthracene
- Benza (a) pyrene
- Naphthalene
- Hexane

The Phase 1 monitor compounds span a molecular weight range of approximately 75 and 350. Available data are also plotted for the log10 of the octanol:water partition coefficient, the log10 of the Henry's constant, and the GAC capacity at exhaustion for an assumed influent concentration of 100 ug/L. The octanol:water partition indicates the hydrophobic nature of a compound, and the more hydrophobic compounds will tend to associate with particulate organic matter and could be removed through coagulation and sedimentation. A roughly inverse relationship exists between octanol:water partition coefficient and the Henry's constant, a measure of volatility. Thus, while some compounds are less hydrophobic, and not likely to be removed through settling of natural organic particulates, they may be removed through aeration.

Pilot plant operation. Once steady-state pilot plant operation is achieved,a spiking solution containing the fourteen monitor compounds will be made up in methanol and fed at a spiking port upstream of the coagulation/flocculation basin, resulting in a diluted concentration of approximately 10 ug/L. At this influent concentration and the expected detection limits of the analytical procedures to be used, removals of approximately 99 percent can be quantified. Samples will be taken for analysis of the raw influent, the spiked influent and the filter effluent.

Evaluation of Organics Removal by Fixed Bed GAC Adsorber

Goal. There are two goals for the second phase of this study. The first is to determine the effectiveness of GAC in removing ambient levels of SOCs from conventionally treated drinking water. The second is to obtain sufficient information to be able to predict the performance of fixed bed GAC contractors, under various scenarios of influent concentrations of SOCs. This requires calibration of the proposed model of multicomponent GAC adsorption.

Compound selection. A similar approach to that described above was taken for selecting Phase II monitor compounds from among the 34 target compounds. Compared to Phase I, however, a smaller number of compounds will be used because the computer can simulate the removal of up to six compounds only. The Phase II monitor compounds chosen are:

- Tetrachloroethene
- Benzene
- 1,2-Dichloroethane
- 1,4-Dichlorobenzene
- alpha-BHC
- Naphthalene

These compounds were chosen to represent a range of physicochemical properties. Because the goal of Phase II operation is to obtain GAC adsorption data, the six compounds were chosen to represent those compounds which may breakthrough a GAC adsorber at least within the time frame of the test period (i.e. 52 weeks).

Pilot plant operation. GAC is very effective in removing a number of the Phase II monitor compounds following conventional treatment. For this reason, the pilot plant will be operated for 1 year in order to observe the breakthrough of strongly adsorbed compounds through the spiked columns.

Since the use of an organic solvent such as methanol would compete with the monitor compounds in the adsorption process, it is proposed that filtered water from the pilot plant be used as the spiking solution solvent. The spiking solution will be pumped from "no-headspace" containers to minimize volatilization of the compounds with higher Henry's constants. The spiking solution flow will be to the port upstream of the two spiking columns. The exact spiking protocol will be determined in the field because of the problems identified with preparation of aqueous spiking solutions.

Because of the high adsorption capacity of GAC for trace levels of the six monitor compounds, GAC column influent concentrations of 1000 ug/L were desired in order to observe breakthrough. Based on the solubilities reported, this column influent concentration can be achieved for four of the six compounds. Concentrations of only 276 ug/L and 558 ug/L can be achieved for alpha-BHC and naphthalene, respectively, because of their low aqueous solubilities. (Note: all calculations using alpha-BHC have been included in this discussion, as beta-BHC has only very recently been selected as a target monitoring compound to replace alpha-BHC.)

Sampling and analysis. To refine the sampling schedule preliminary GAC adsorption modelling runs were made for the pilot plant operating conditions by Dr. John Crittenden's group at Michigan Technological University.

Detailed discussion of the homogeneous surface diffusion model (HSDM), the equilibrium column model (ECM) and the ideal adsorbed solution theory (IAST) can be found elsewhere (Crittenden, 1985). A brief summary is given here.

The HSDM describes the fate of an adsorbate within a fixed-bed adsorber. It incorporates the mechanisms of advective flow, liquid-phase mass transfer resistance, local adsorption equilibrium at the exterior surface of the adsorbent, surface diffusion, and competitive equilibrium of solutes upon the carbon surface. The ECM divides the fixed bed into zones of constant composition that expand and move down the bed as solute accumulates on the adsorbent. The ECM defines the elution order of adsorbates, the highest overshoot concentration, the number of bed volumes that may be treated before the highest overshoot may occur, and the lowest GAC usage rate. Results from the ECM closely approximate actual breakthrough data for long columns, such as the 20 minute overall EBCT studied here.

Successful model predictions are dependent on good descriptions of multicomponent equilibria and mass transfer rates. The competitive equilibrium adsorption effects of multi-solute systems is estimated using IAST. This approach corrects the single solute isotherm for the competitive effects of other compounds in solution, since the presence of a more strongly adsorbing compound can reduce the degree of adsorption of a weaker adsorbing compound. The mass transfer parameters of film transfer coefficient, the surface diffusion coefficient, and pore diffusion coefficient describe the mass transfer rate and can be determined by thermodynamic correlations. The Freundlich capacity parameter and the Freundlich intensity parameter must also be determined for each adsorbing species.

Using the modified isotherms as determined by IAST for the six monitor compounds, the bed volumes treated until breakthrough can be estimated using ECM. Multiplying the bed volumes treated by the EBCT yields the time to breakthrough. The results of these calculations are listed in Table 2 for influent concentrations of 10, 100 and 1000 ug/L and EBCTs of I, 10 and 20 minutes. The six monitor compounds are predicted to breakthrough in the order 1,2-dichloroethane, 1,4-dichlorobenzene, benzene, naphthalene, tetrachloroethane and alpha-BHC. The results illustrate the importance of using column influent concentrations of close to 1000 ug/L to observe breakthrough for at least a 10 minute EBCT within the year period for all compounds.

TABLE 2 Equilibrium Predictions of Breakthrough Times

	Empty Bed Contact Time (EBCT)		
	1 min	10 min	20 min
alpha-BHC			
1000 ug/l=C_o	46 d	465 d	929 d
100	156	1563	3126
10	503	5030	10060
Tetrachloroethene			
1000 ug/l	21	210	420
100	90	900	1800
10	355	3549	7098
Napthalene			
1000 ug/l	23	230	460
100	80	800	1600
10	268	2682	5364
Benzene			
1000 ug/l	18	180	360
100	46	460	920
10	204	2036	4073
1,4-Dichlorobenzene			
1000 ug/l	10	100	200
100	45	450	900
10	185	1848	3696
1,2-Dichloroethane			
1000 ug/l	4	40	80
100	6	60	120
10	8.5	85	170

To account for the effects of mass transfer in the adsorption columns, the plug flow homogeneous surface diffusion model (PFHSDM) was used. The results of these two modelling runs for the predicted breakthrough of the six Phase II monitor compounds are plotted in Figure 1 and Figure 2. The breakthrough curves were calculated using the equilibrium isotherm parameters determined above. A water temperature of 13.8°C was assumed for both runs. Figures 1 and 2 contain plots of the breakthrough curves in one minute and ten minute EBCT columns, respectively. The model runs for the twenty minute EBCT column as influent concentration of 1000 ug/L were not successful. Modifications are in progress to resolve the numerical imitations encountered.

To simplify the modelling, the breakthrough behaviour of naphthalene was assumed to be similar to tetrachloroethene as their predicted equilibrium parameters were approximately equal. The column effluent concentration was normalized by dividing the actual effluent concentration by the influent concentration of 1000 ug/L. To separate the individual breakthrough curves more clearly, the time scale is plotted logarithmically. Although the five compounds breakthrough then column in the same relative order as predicted by equilibrium theory, the time to breakthrough (i.e. time at C/Co = 0.5) is less when accounting for mass transfer effects within the column, as was expected.

Based on these results, the proposed sampling times for the one minute EBCT column are shown as labelled vertical lines in Figure 1.

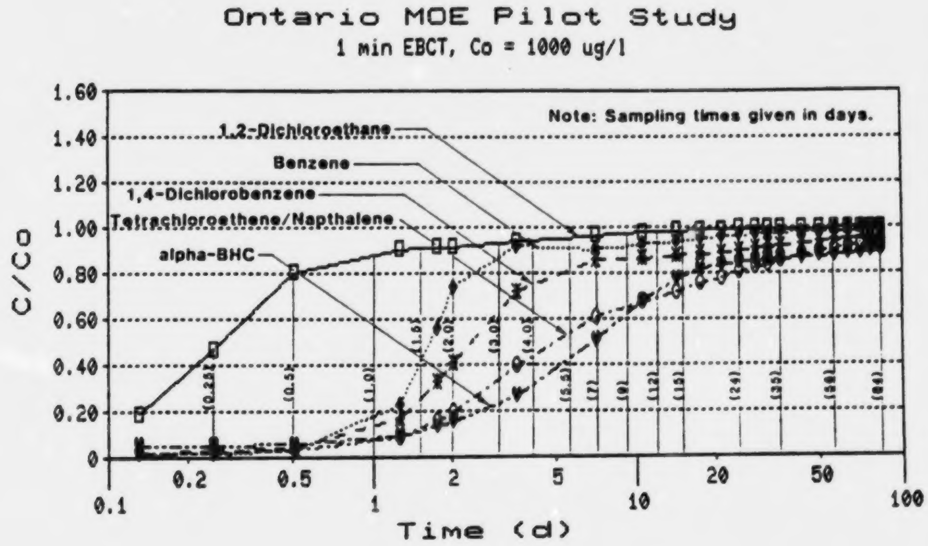


Fig. 1 HSDM 1 min. predicted breakthrough curves

The breakthroughs of the five modelled compounds in the ten minute EBCT column are plotted in Figure 2. The effects of competitive adsorption are more pronounced in this column as evidenced by the breakthrough curves of 1,2-dichloroethane and benzene. These compounds are both weakly adsorbed and breakthrough the column relatively quickly. As the other, more strongly adsorbed compounds are removed on the carbon, the dimensionless effluent concentration of 1,2-dichloroethane and benzene rises beyond 1.0, an indication of chromatographic effects.

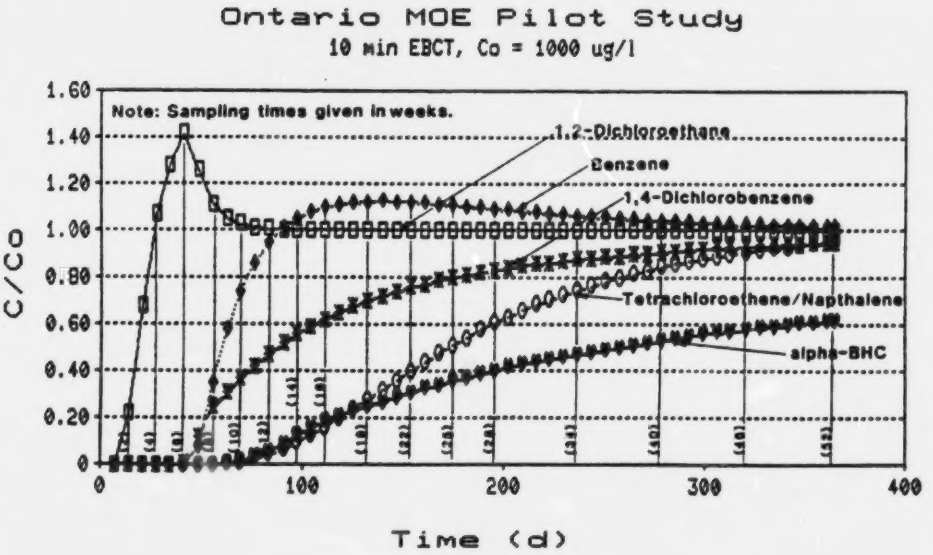


Fig. 2 HSDM 10 min. predicted breakthrough curves

Similar to Figure 1, the proposed sampling times for the ten minute EBCT column are shown as labelled vertical lines in Figure 2.

Figure 3 summarizes the sampling times for all three EBCTs. The sampling frequency for the 20 minutes EBCT column is shown in the lowest timeline.

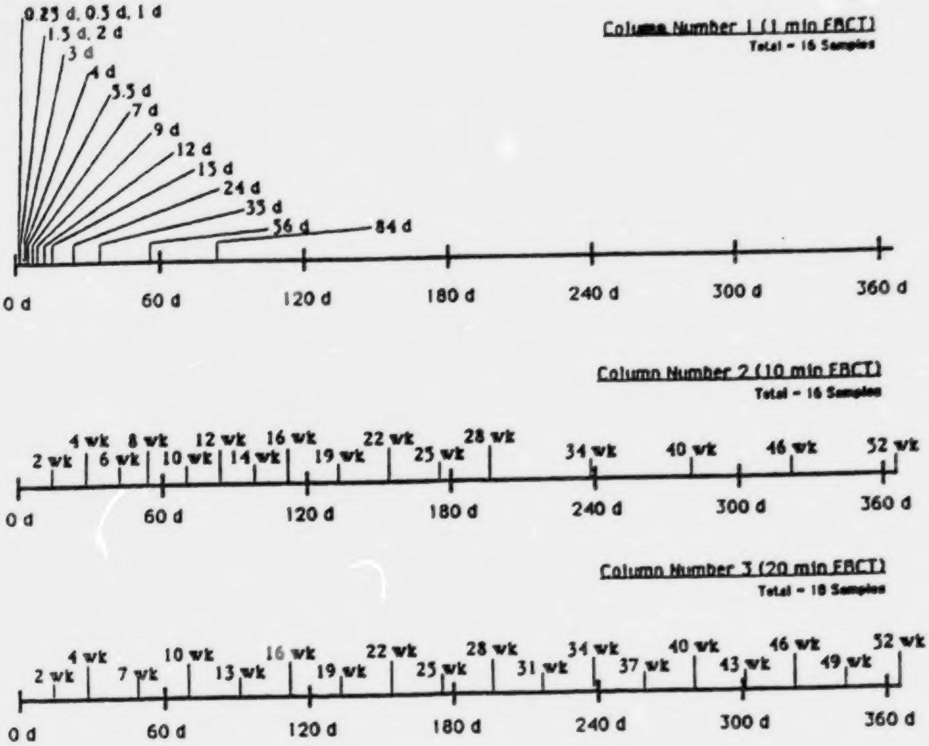


Fig. 3 Spiked GAC column sampling times

PILOT PLANT DESIGN

General Configuration and Materials of Construction. The pilot plant will model a complete water treatment process consisting of flash mixing and coagulation, flocculation, sedimentation and filtration, followed by granular activated carbon adsorption. A single treatment train is provided through filtration. After filtration there are four parallel adsorption process trains, 2 of which serve as backup, i.e. each process train is replicated once. A simplified flowsheet is shown in Fig. 4.

The first process train consists of a single adsorption vessel with a 20 minute empty bed contact time (EBCT). The second process train has three adsorption beds operating in series with EBCT of 1 minute, 9 minutes and 10 minutes each respectively.

The materials of construction as well as process equipment and instrumentation have been carefully selected so that all water-contacting surfaces throughout the entire delivery and treatment processes are of chemically inert substances (i.e. glass, teflon and stainless steel). The design criteria for the various unit processes are described below.

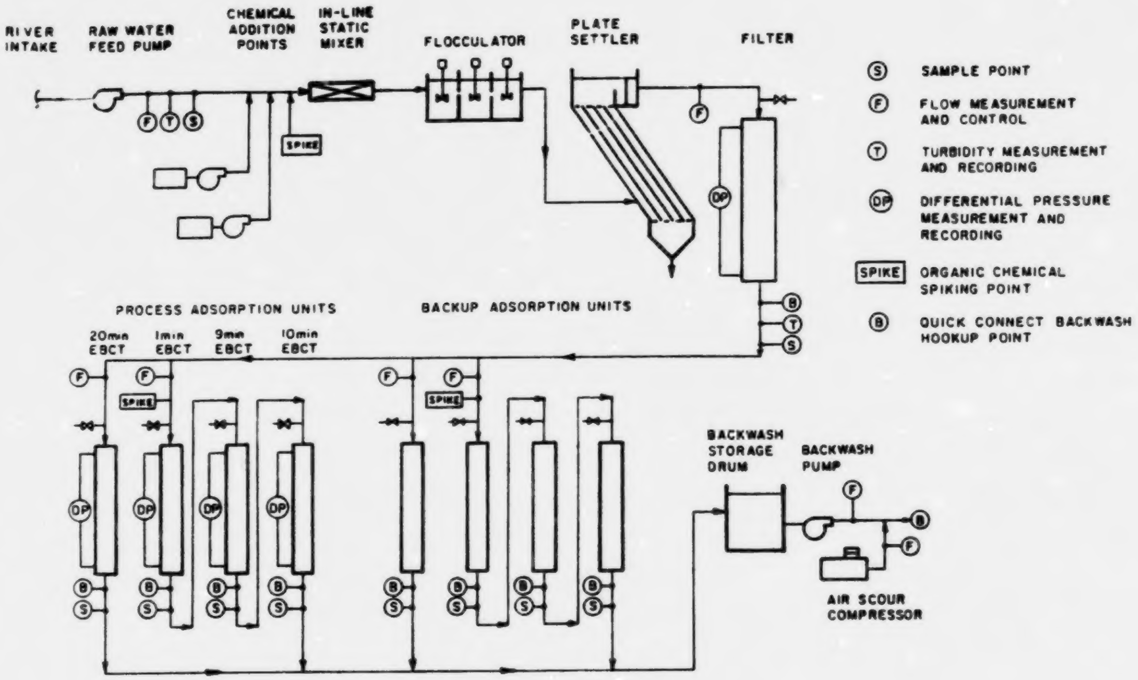


Fig. 4 Simplified pilot plant flowsheet

Raw water supply. The pilot plant is supplied with raw water from the Niagara River through the Niagara Falls Water Treatment Plant's intake system. The draw-off point is in the influent conduit after the travelling screens, but prior to the low lift suction well and the prechlorination and powdered activated carbon addition points. A dedicated stainless steel pump and supply line deliver raw water to the pilot plant, located in the low lift pumping station.

Flash mixing. Flash mixing for both the addition of coagulants, filter-aid and organic spiking compounds is done with an 8 stage Komax-type static mixer.

Flocculation. The flocculator is designed for a 3.8 L/min (1 U.S. gpm) flow. It is divided into 3 compartments, each of which has a hydraulic detention time of 10 minutes. Each compartment has an individually controlled stirrer capable of producing an energy input in the range of $G = 5$ to 30 sec^{-1}.

Sedimentation. The sedimentation process occurs in a lamella clarifier. The lamella plates are 244 cm (8 ft) long and are inclined at an angle of 55 degrees to the horizontal. The plate separation is 5.1 cm (2 inches) and plate width is approximately 23.5 (9½ inches). The overflow rate of the lamella clarifier is 4.75 m/hr (2,840 gpd/ft^2).

Filtration. The filter is a 10.2 cm (4 inch) diameter column, 305 cm (10 feet) high. It is constructed from glass pipe and capped with 304 stainless steel flanges. The lower flange has a built-in plenum with a flow divider plate and stainless steel media retainer. The filter will operate at a flowrate of 12.2 m/hr (5 gpm/ft^2), and will use the same media used currently at the Niagara WTP.

Carbon adsorption. The carbon adsorption contact vessels are constructed exactly as the filter with the exception that they are 7.6 cm (3 inches) in diameter. At the empty bed contact times stated above, the flow rate through each adsorption train is 0.237 L/min (0.0625 U.S. gpm).

Instrumentation. A recording turbidimeter is installed at two points in the pilot plant. These are at the entrance point for the raw water and at the filter effluent. Filter head loss is measured by a differential pressure (DP) cell. There are also DP cells on four of the eight carbon adsorption vessels. As with the turbidimeters, the DP cells are outfitted with strip chart recorders.

Organic spiking points. Spiking points for organic chemicals are located at the entrance to the flocculator and in the filter effluent, upstream of the two carbon adsorption process trains which consist of the three adsorption vessels in series.

Sampling points. Sample valves in the pilot plant are located on the raw water supply, the filter effluent and at the end of each carbon adsorption vessel. In addition, samples may be taken from the free water surfaces in the flocculator and the sedimentation tank.

DATA ANALYSIS

At the simplest level the organics removal data generated during Phases I and II will indicate the effectiveness of the chosen treatment train in removing ambient concentrations of SOCs. Based on the currently available water quality data with respect to SOCs, the conventional water treatment processes followed by GAC fixed bed adsorbers are expected to remove all the monitor compounds at their ambient concentrations. Although useful as demonstration, operation under these conditions for the limited period of the pilot plant study yields little information on GAC costs (i.e. the impact of EBCT on GAC usage rate and regeneration frequency) and the ability of the GAC columns to act as a barrier against shock loads of SOCs as would occur following a spill.

The data obtained from the spiked GAC adsorption columns will be used to evaluate both these issues. Because the elevated SOC concentrations in the spiked filtered water are expected to cause breakthrough in at least one of the columns, the breakthrough curves can be used to calibrate the mass transfer adsorption model. procedure which uses a combination of the ECM and the HSDM has been developed to simplify mass transfer model calculations by reducing the number of components that need to be considered in multicomponent mass transfer calculations. Assuming that the effects of ambient DOC concentrations on the adsorption of varying concentrations of SOCs and of the competitive adsoption of a number of SOCs can be evaluated, the model will be useful for several purposes.

First, the model can be used to estimate the breakthrough of DOC and SOCs at their ambient concentrations in order to set regeneration criteria. The ambient concentration depends on the effectiveness of the upstream processes. Thus, the organic loading on the carbon columns have varying ratios of DOC to SOCs. The associated operating costs could then be calculated, assuming this were the primary function of GAC contactors.

If the primary function of GAC contactors were instead to provide a barrier against temporry high concentratios of SOCs, as would occur during a chemical spill, the model could be used to help evaluate operating criteria. At ambient concentrations, DOC would provide the greatest loading on the carbon columns. The model could be used to evaluate the adsorption capacity remaining as a function of time. Note that the adsorption capacity remaining would also depend on the characteristics of the spilled chemical. The wide range of physiochemical characteristics of the SOCs used in Phase II will provide useful data for evaluating a number of spill scenarios.

REFERENCES

City of Toronto, Department of Public Health (1954). Toronto's Drinking Water: A Chemical Assessment.

Crittenden, J.C. and colleagues (1985). Design of Fixed-Beds to Remove Multicomponent Mixtures of Volatile Organic Chemicals. Presented at 1985 AWWA Meeting, June 23-27, at Washington, D.C.

International Joint Commission (1983). Report to the Great Lakes Water Quality Board; An Inventory of Chemical Substances Identified in the Great Lakes Ecosystem. Vol. I.

Municipality of Metropolitan Toronto, Department of Public Works (1983). Water Test Data, 1971-1983.

Niagara River Toxics Committee (1984). Report of the Niagara River Toxics Committee.

New York Public Interest Group (1981). The Ravaged River.

Ontario Ministry of the Environment (1984). Drinking Water Survey of Selected Municipalities in the Niagara Area and Lake Ontario.

Ontario Ministry of the Environment and Environment Canada (Canada-Ontario Review Board) (1985a). Trace Organics in Ontario Drinking Water Along the Niagara River.

Ontario Ministry of the Environment (1985b). Data from MOE routine monitoring program of raw and treated water in the Niagara Falls area, 1978 to 1985.

First presented at the 2nd National Conference on Drinking Water, Edmonton, Alberta, April 1986.

THE ROLE OF ORGANIC CARBON IN CONTROLLING THE OCCURRENCE OF DENITRIFICATION IN GROUNDWATER

R.C. Starr and R.W. Gillham

Institute for Groundwater Research
Department of Earth Sciences
University of Waterloo
Waterloo, Ontario

BACKGROUND

Nitrate is recognized as the most commonly identified groundwater contaminant (Freeze and Cherry, 1979). Decomposition of plant and animal matter, such as from barnyards and sewage disposal facilities, may result in high concentrations of nitrate in groundwater. Widespread nitrate contamination often results from the use of agricultural fertilizers. Groundwater provides drinking water in many agricultural areas, but extensive nitrate contamination can make obtaining a supply of drinking water with nitrate concentrations below the 10 mg-N/l drinking water standard difficult. Mechanisms that control nitrate concentrations in groundwater are therefore of considerable practical importance in areas where nitrate contamination is common.

Denitrification, the process by which some bacteria convert nitrate (NO_3^-) into nitric oxide (NO), nitrous oxide (N_2O) and molecular nitrogen (N_2), lowers nitrate concentrations and can therefore reduce nitrate contamination problems.

FIELD EVIDENCE OF DENITRIFICATION IN GROUNDWATER

Previous studies conducted by the University of Waterloo have shown that denitrification occurs in some aquifers beneath agricultural land in southern Ontario. Gillham and Cherry (1978) interpreted geochemical profiles from several sites as indicating that denitrification was responsible for decreasing nitrate concentrations with depth. Trudell et al. (1985) describe an experiment in which groundwater spiked with nitrate was injected into a shallow aquifer. Nitrate concentrations declined more than could be attributed to dilution, and the population of denitrifiers increased over the course of the experiment. These results, coupled with changes in other geochemical parameters, indicate that denitrification occurred at this site. Although these studies indicate that denitrification occurs in groundwater in some settings, it is not an important mechanism in many outer aquifers. Gillham and Cherry (1978) also describe an aquifer where denitrification did not appear to occur, and the common occurrence of nitrate-contaminated groundwater suggests that denitrification does not occur, of at least that the denitrification rate is less that the rate of nitrate input, in many aquifers. An understanding of the factors that control the rate of denitrification in groundwater is required in order to predict trends in nitrate contaminated aquifers, and may provide insight into effective aquifer renovation schemes.

Two field sites in southern Ontario were characterized to develop an understanding of factors that control the occurrence and rate of denitrification on groundwater. Both sites are on the edge of active agricultural fields and receive regular applications of nitrogen fertilizer. Each is underlain by a sandy, unconfined aquifer. Figure 1a shows geochemical profiles at the field site near Rodney, Ontario. Nitrate and chloride are believed to be derived from agricultural fertilizer, and the presence of chloride throughout the profile at fairly uniform concentrations suggests that fertilizer derived solutes were present throughout the section. The marked decline in nitrate from 25 mg-N/l to less than the 0.3 mg-N/l detection limit over a vertical distance of 0.5 metre and within 1.5 metres of the water table suggests that denitrification is an active process at this site. This is in agreement with Trudell et al. (1985), who performed their injection experiment here. In contrast, nitrate persists for nine metres below the water table and closely parallels chloride concentration at the field site near Alliston, Ontario (Figure 1b). This indicates that denitrification was not occurring at an appreciable rate in groundwater at this site.

LAB RESULTS

Denitrification is performed largely by heterotrophic bacteria that reduce nitrate and oxidize organic carbon to gain energy. The reaction may be represented in a gross sense by

$$5\ C + 4\ NO_3^- + 2\ H_2O \Rightarrow 5\ CO_2 + 2\ N_2 + 4\ OH^-$$

where C represents organic carbon. This shows that the mass of organic carbon consumed during denitrification is comparable to the mass of nitrate reduced to nitrogen, and therefore that the availability of organic carbon can influence the amount of nitrate that can be denitrified.

A major difference between the physical characteristics of the two field sites is the depth to the water table. It is at a depth of about one metre at Rodney, but at about four metres at Alliston. Gillham and Cherry (1978) observed a pattern similar to the one shown an Figure 1, in that denitrification appeared to occur in aquifers with a water table only one or two metres below ground surface, but not to occur in aquifers with a deeper water table. They hypothesized that water table depth could influence the flux of organic carbon from the overlying unsaturated zone into the saturated zone. Oxidation of organic carbon to carbon dioxide reduces the mass of organic carbon as it is transported downward from the topsoil horizon to the underlying aquifer, so in general the flux of organic carbon into shallow water table aquifers would be expected to be greater than into deeper water table aquifers.

Figure 2 shows the concentration of dissolved organic carbon (DOC) in pore water and solid phase organic carbon (F_{oc}) at Rodney. Both profiles show that the topsoil (0-0.3 m) is a large reservoir of organic carbon. Concentrations are much lower between the topsoil and the watertable (1 m) and still lower below the watertable. In general, water at greater depth in this system has had a longer residence time, so decreasing concentrations with depth is consistent with oxidation of organic carbon during transport.

The ability of materials from various depths at Rodney to support denitrification was determined in the laboratory. The acetylene inhibition technique (Tam and Knowles, 1976) was used, in which the concentration of nitrous oxide is proportional to the mass of nitrate denitrified. Figure 3 shows the experimental results. The control case shows little systematic variation with depth. Samples that were spiked with nitrate show much more denitrification the that the control case in the upper metre, indicating that denitrification in the laboratory was limited by low nitrate availability. This is not suprising, since the cores used in this work were collected after the growing season and long after fertilized application. The denitrification rate was quite high in samples from the organic carbon rich topsoil horizon and generally lower in the vadose zone below the topsoil, and still lower below the water table. Below one metre depth there was little difference between the control and nitrate-amended samples, indicating that denitrification in these samples was not nitrate limited. A third suite of samples was spiked with both nitrate and glucose, a readily available organic carbon source for bacteria. The data for these samples coincide with those from the nitrate amended samples to a depth of one metre, indicating that abundant organic carbon was present. At greater depths, denitrification was enhanced by the addition of glucose, indicating that although sufficient organic carbon to support denitrification was present, the denitrification rate was limited by organic carbon availability.

The results of similar work with samples from Alliston are shown on Figure 4. Denitrification in the control case was high at shallow depths and generally decreased with increasing depth. Denitrification was not observed in samples collected below two metres, and addition of nitrate did not stimulate denitrification. Glucose addition caused a substantial increase in the observed denitrification rate at all depths, indicating that the availability of organic carbon was limiting. In particular, addition of glucose to samples from greater than two metres depth caused denitrification to occur, which contrasts sharply with the lack of denitrification in these samples when glucose was not added. This clearly indicates that low availability of organic carbon inhibited denitrification in these samples.

The results from the laboratory support the hypothesis that the available mass of organic carbon decreases with depth, and that denitrification does not occur in groundwater at Alliston because too little organic carbon is available.

FIELD RESULTS

The rate of denitrification was measured insitu at both field sites as an independent measure of the importance of organic carbon. As in the laboratory work, the mass of nitrous oxide is proportional to the mass of nitrate denitrified.

Figure 5a shows the results of the control case at Rodney. The decline in nitrate coupled with the production of nitrous oxide clearly shows that denitrification occurred. This demonstrates that denitrification occurs under natural conditions at Rodney, and that there is sufficient organic carbon to support denitrification. A second treatment was used, in which glucose was added. Figure 5b shows that the denitrification rate was echanced by the addition of a readily usable source of organic carbon. The measured dissolved organic carbon concentrations show that the glucose was consumed between 2 and 4 days. The denitrification rate during the period when glucose was utilized was 1200 mg-N/l/year, and declined to 260 mg-N/l/year afterwards, which is quite close to the 210 mg-N/l/year observed in the control case. This indicates that sufficient natural organic carbon to support denitrification was present at Rodney, but that the rate was controlled by organic carbon availability. This agrees with the results of the laboratory investigation.

Figure 6 shows the results of similar experiments at Alliston. Denitrification was not observed in the control case, but did occur in the glucose-amended case. This shows that denitrification did not occur in the control case due to an insufficient supply of organic carbon, and is also in agreement with the laboratory results.

SUMMARY

Groundwater at both Rodney and Alliston is contaminated with nitrate at concentrations above the drinking water limit. Denitrification at Rodney consumes nitrate and nitrate concentrations fall rapidly with depth, so that only the upper 1.5 metres of the aquifer is contaminated with nitrate.

Denitrification does not occur at the Alliston field site, and high concentrations of nitrate persist for 8 metres below the watertable. This clearly shows the importance of denitrification in mitigating contamination of groundwater beneath agricultural land.

The experimental results show the importance of organic carbon availability on the occurrence and rate of denitrification in groundwater. Oxidation of organic carbon during transport through the unsaturated zone influences the organic carbon flux into the saturated zone. The insitu experiments at Alliston show that denitrification can be induced by the addition of labile organic carbon, which suggests that it may be possible to renovate some nitrate contaminated aquifers by stimulating denitrification with the addition of labile organic carbon.

REFERENCES

1 Freeze, R.A., and J.A. Cherry, 1979. Groundwater. Prentice-Hall, Englewood Cliffs.

2 Gillham, R.W., and J.A. Cherry, 1978. 'Field Evidence of Denitrification in Shallow Groundwater Flow Systems', Water Pollution Research Canada, 13, 53-71.

3 Tam, T.V. and R. Knowles, 1976. 'Acetylene Inhibition of Nitrous Oxide Reduction by Denitrifying Bacteria', Biochemical and Biophysical Research Communications 69(3) 705-710.

4 Trudell, M.R., R.W. Gillham and J.A. Cherry, 1985. 'An Insitu Study of the Occurrence and Rate of Denitrification in a Shallow Unconfined Sand Aquifer', submitted to the Journal of Hydrology.

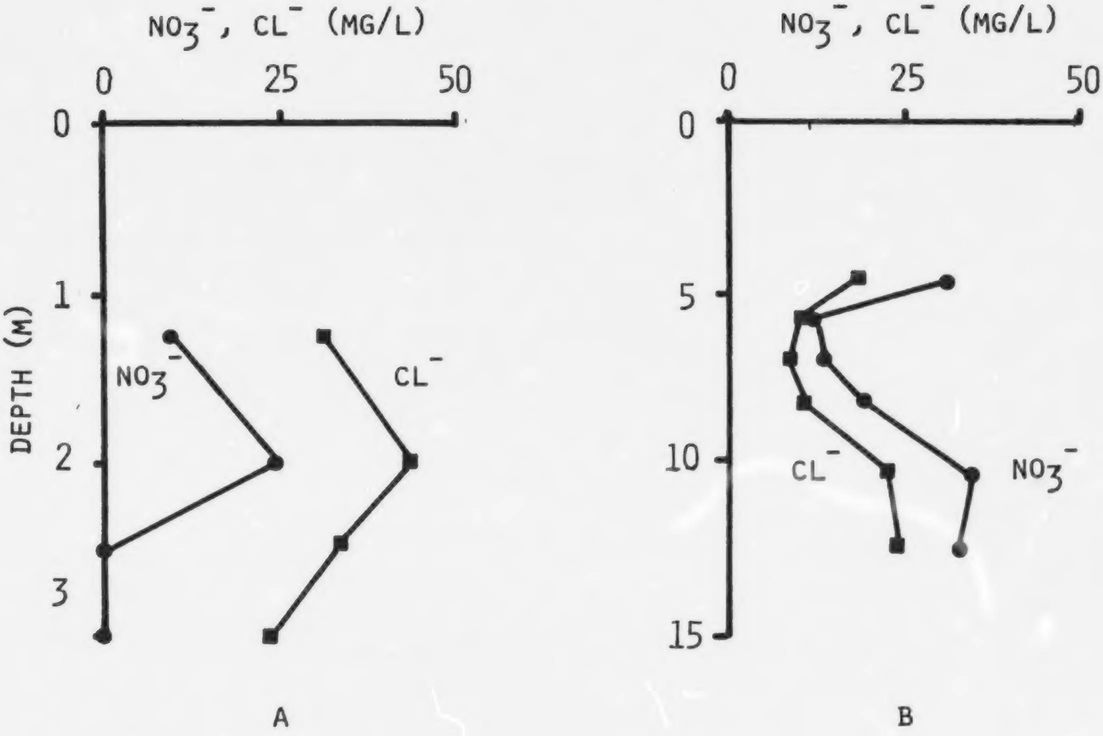


FIGURE 1
GEOCHEMICAL PROFILES
(A) RODNEY
(B) ALLISTON

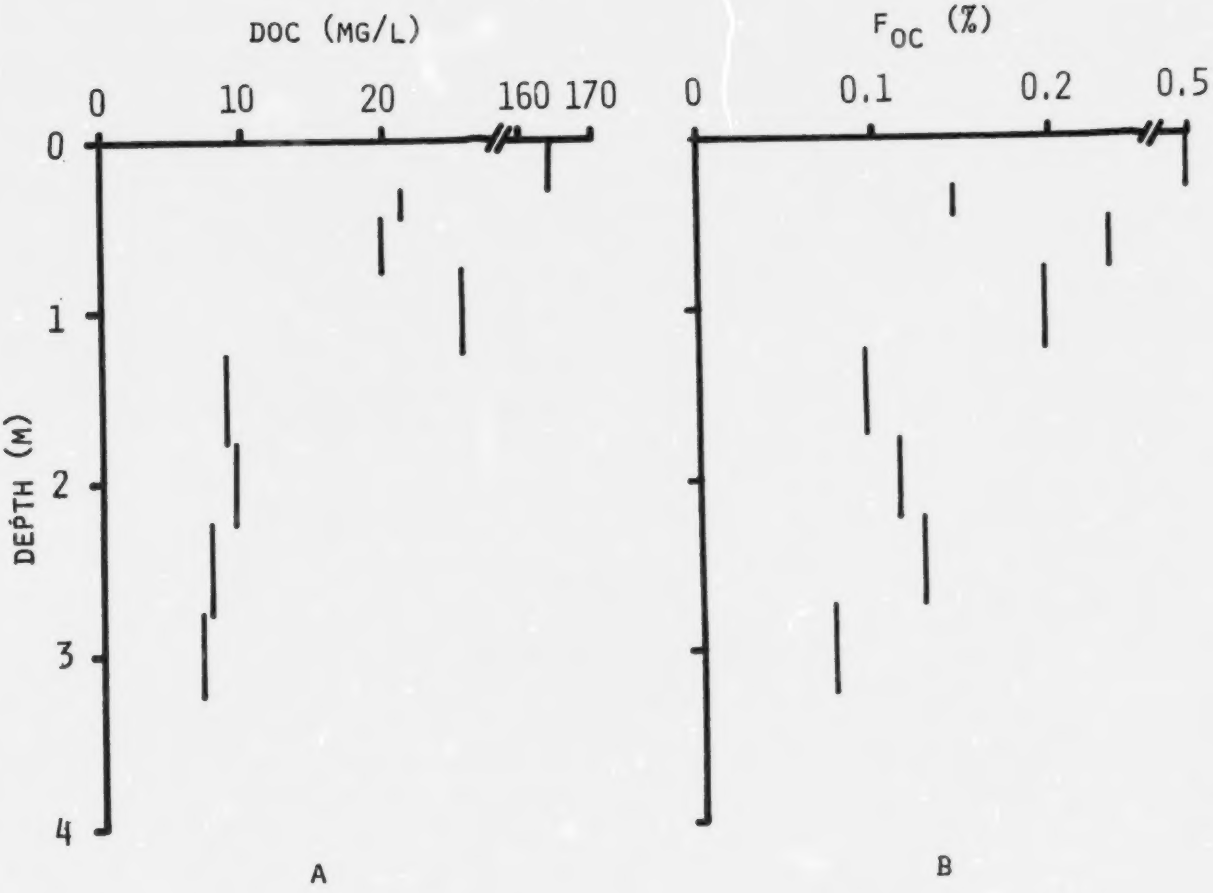


FIGURE 2
(A) DISSOLVED ORGANIC CARBON IN RODNEY POREWATER
(B) SOLID ORGANIC CARBON IN RODNEY SEDIMENT

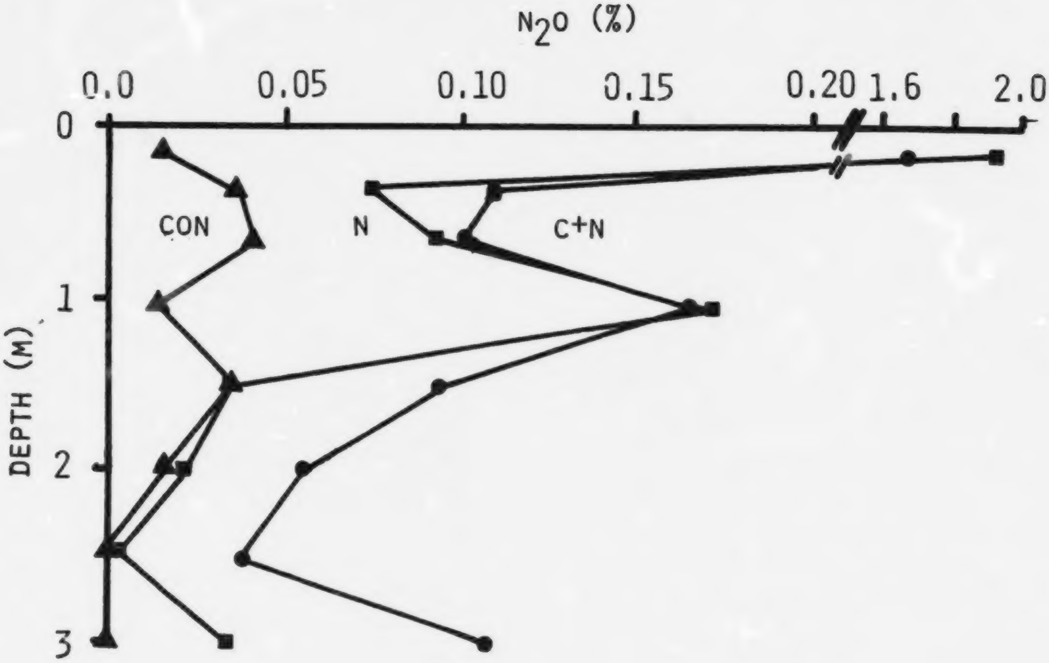


FIGURE 3
LABORATORY DENITRIFICATION TEST
RODNEY MATERIALS

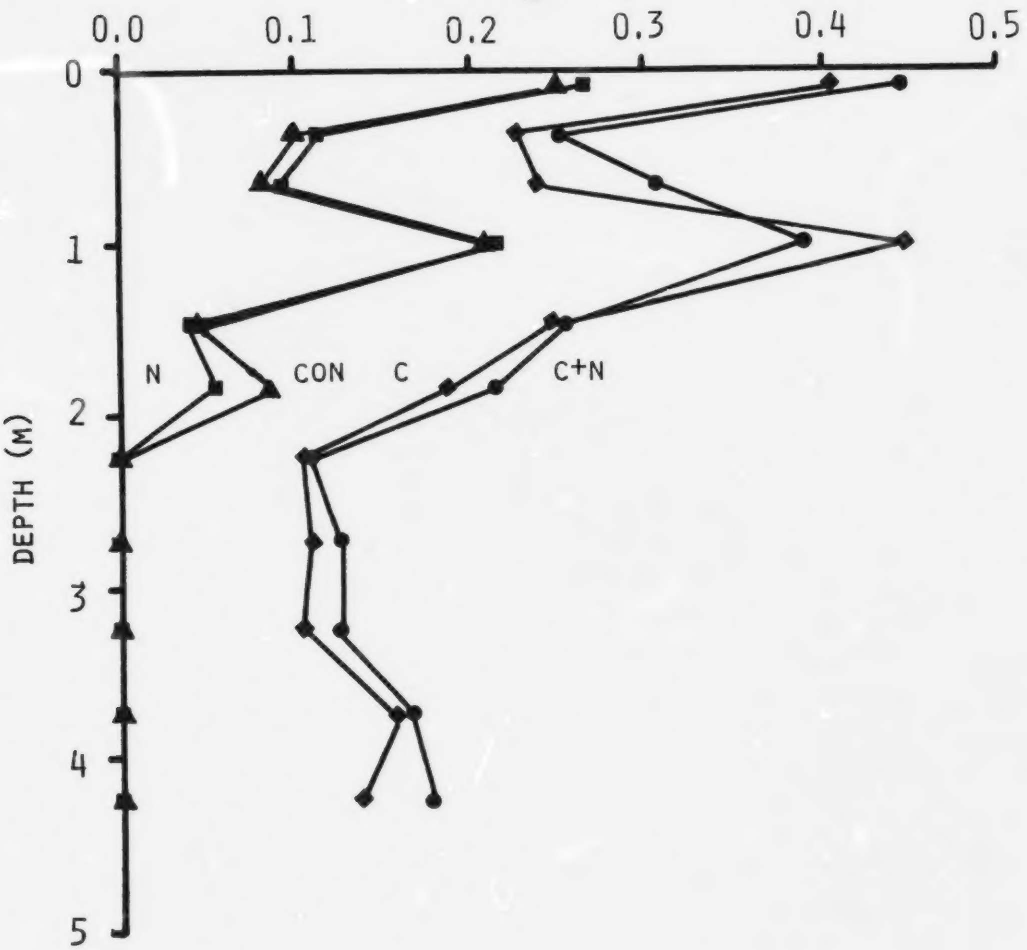


FIGURE 4
LABORATORY DENITRIFICATION TEST
ALLISTON MATERIALS

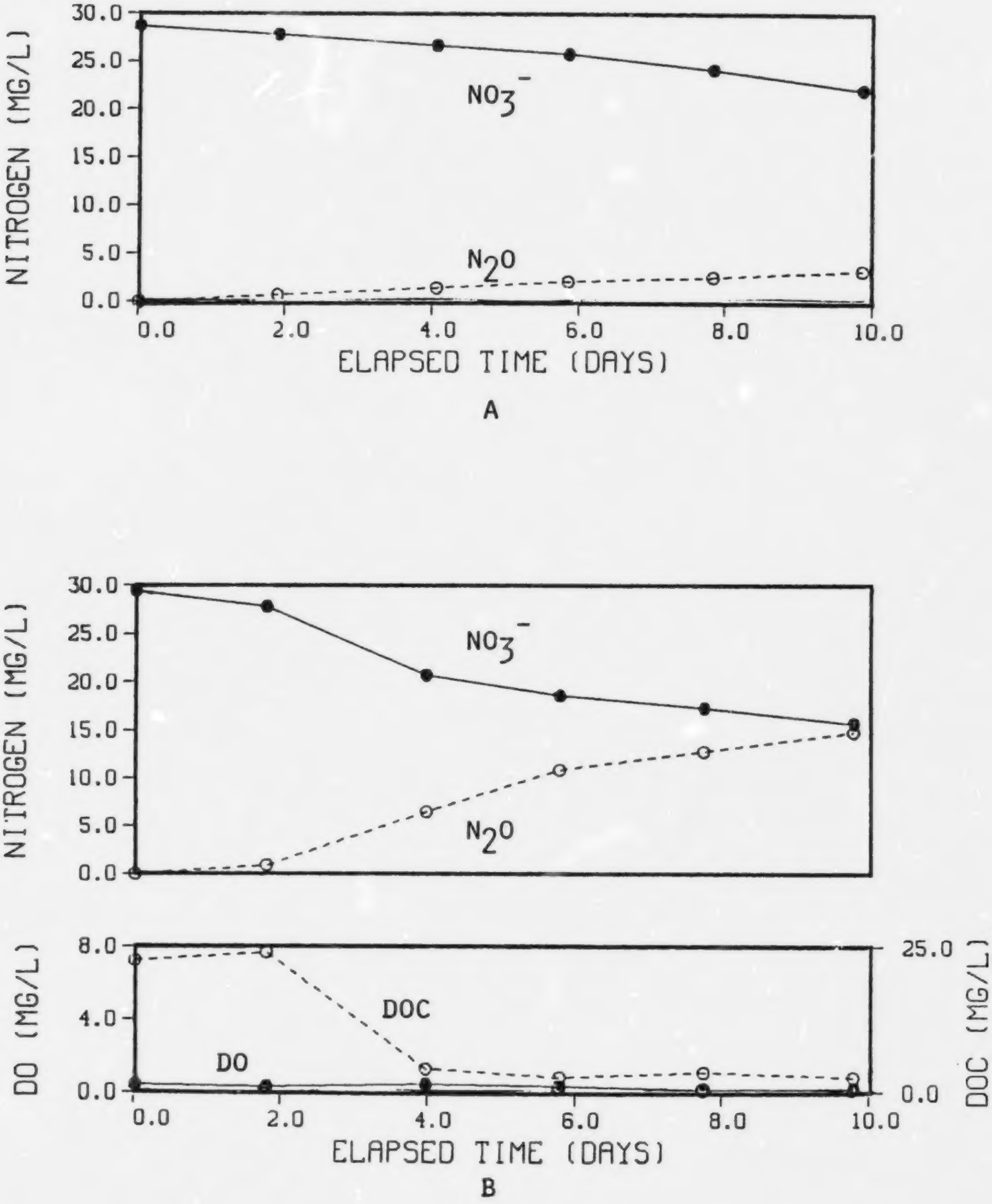


FIGURE 5
RODNEY INSITU DENITRIFICATION
(A) CONTROL
(B) GLUCOSE AMENDED

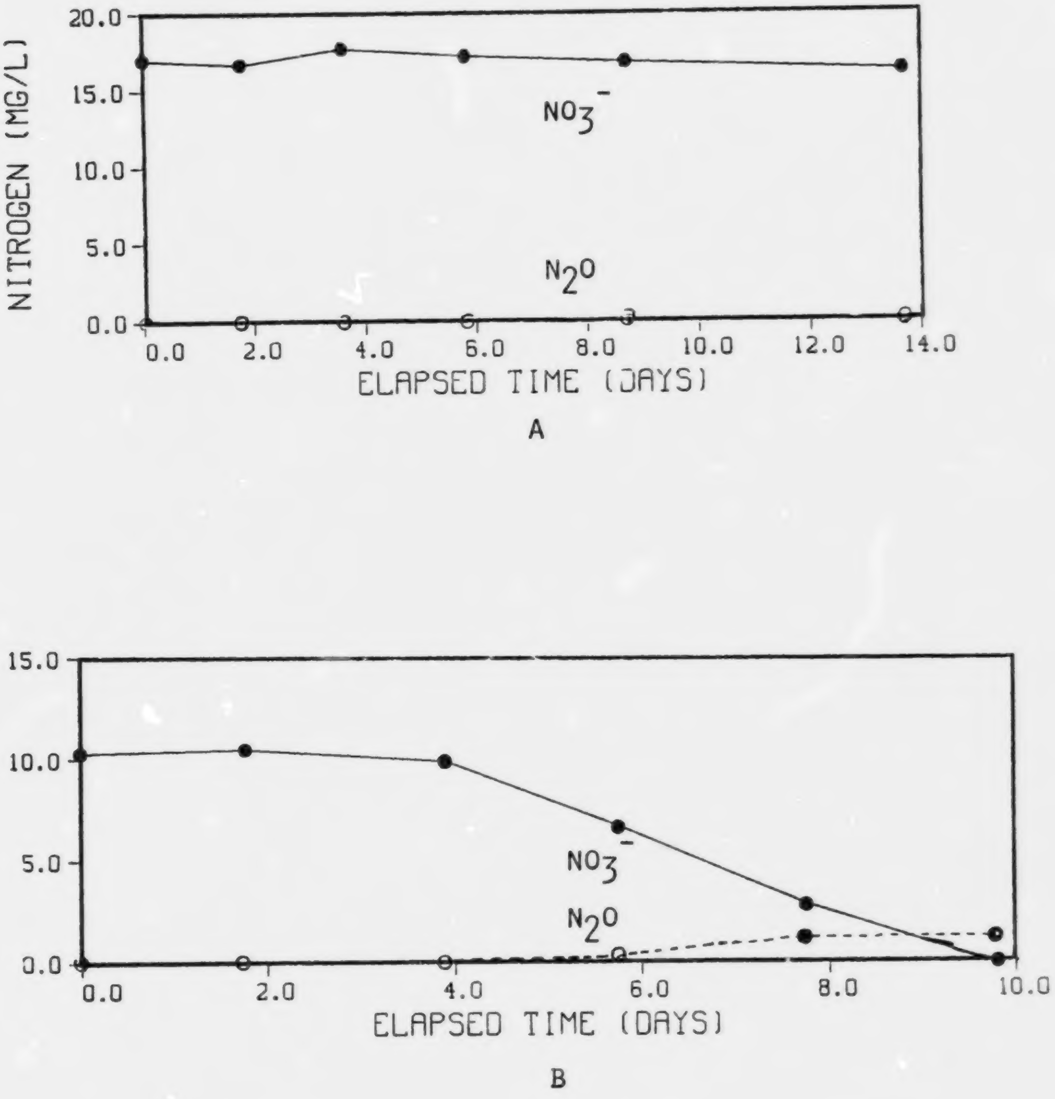


FIGURE 6

ALLISTON INSITU DENITRIFICATION

(A) CONTROL

(B) GLUCOSE AMENDED

REPRODUCTIVE OUTCOMES IN SOUTHWESTERN ONTARIO, 1980 TO 1985

James McD. Robertson, D.V.M, M.Sc.(Med.)[1]
Harvey J. Chan, M.D.[2]

[1] Associate Professor, Department of Epidemiology and Biostatistics, Faculty of Medicine, University of Western Ontario, London, ON, N6A 5C1

[2] Graduate Student.

Presented at the 1986 Technology Transfer Conference, Toronto, December, 1986.

ACKNOWLEDGEMENTS

This project was supported by the Ontario Ministry of Health and The Ontario Ministry of the Environment.

The assistance of Drs. L.F. Smith, P.R.W. Kendall and R. Khazen and Mrs. C. Ragos of the Ministry of Health is gratefully acknowledged as is that of Mrs. R. Gage, D. Georgas and J. Workman of the Office of the Registrar General.
Dr. G.J. Sherman of the Canadian Congenital Anomalies Surveillance System provided the data on congenital anomalies. This project would not have been possible without the support and cooperation of Dr. W.A. Everett, Medical Officer of Health, Kent-Chatham Health Unit and Dr. L.M.C. Duncan, Medical Officer of Health, the Lambton Health Unit.

INTRODUCTION

The spills of various toxic substances into the St. Clair River during the six year period, 1980 to 1985, with the potential contamination of drinking water in certain communities has caused understandable concern among both the residents and the Medical Officers of Health in Kent and Lambton Counties. Although no acute effects have been documented to date, the possibility of adverse effects in pregnant women and their children cannot be ignored. Unlike neoplastic and other chronic diseases, adverse reproductive and first-year-of-life outcomes could provide a highly sensitive, rapidly-occurring and easily documented sentinel measure of the risk of exposure to potentially contaminated drinking water in these counties. With this in mind, the Ontario Ministry of Health issued a call for proposals for epidemiologic studies in early 1985. The study described here was designed to document the presence/absence and extent of the risks of abnormal pregnancy and first-year-of-life outcomes in women and their children whose source of drinking water during the six year period, 1980 to 1985, was the St. Clair River.

METHODS

The study has three phases: an ecologic study, a case-control study, and a retrospective, special exposure cohort study. Drinking water drawn from the St. Clair River is the primary exposure of interest. The outcomes selected for study are listed in Table I.

1. Ecologic study

This phase of the study will compare the incidence rates of the abnormal outcomes during the six year period, 1980 to 1985, in Kent and Lambton Counties with those of the Ontario Southwest Region (Bruce, Elgin, Essex, Grey, Huron, Kent, Lambton, Middlesex, Oxford and Perth Counties) and with those of the Province to determine if any of the outcomes occurred in excess in the index counties. Comparisons will also be made between exposed and unexposed groups, defined by geographic location, within Kent and Lambton Counties.

Six year total incidence rates will be calculated from data supplied by the Ontario Ministry of Health. The comparisons will be based on relative risks estimates with corresponding 95 per cent confidence limits.

2. Case-control study

This phase will focus on stillbirths, congenital anomalies, low birth weight ($\leq$ 1,500 gm.) and first-year-of-life outcomes which occurred between 1 January, 1980 and 31 December, 1985. We excluded spontaneous abortions because the number, almost 800 in 1980 to 1984, was too large to include in an interview study given the time frame and funding of the project. Taking into account combined diagnoses for example, stillbirth and congenital anomaly, we estimate that some 500 cases will be eligible for interview.

The controls will be a group of women from Kent and Lambton Counties who had normal babies in the same time period or whose children were normal and survived beyond the first year of life. Control mothers will be individually matched to case mothers on maternal age (± 1 year), parity, multiple birth and sex of the child.

Cases and controls will be interviewed at home using a pre-tested interview schedule to gather information on the variables listed in Appendix 1.

The primary analysis will concentrate on case-control differences in exposure to drinking water from the St. Clair River. Comparisons of frequencies will be made using the marginal Chi square test. The effects of confounding variables will be controlled by stratification or paired multiple logistic regression analysis where appropriate. Since this is a population-based case-control study, it will also be possible to calculate relative and attributable risks directly from the data.

3. Retrospective, special exposure cohort study

Some 40 chemical spills into the St. Clair River between 1980 and the end of 1985 have been documented. We have selected six such spills (Table II), on the basis of time period, material spilled and amount spilled, for further study. Using spontaneous abortions, stillbirths, congenital anomalies and low birth weight, we shall attempt to estimate the influence of these spills on outcomes of pregnancy.

A cohort of women who were pregnant at the time of these spills and, based on place of residence, were considered to be exposed will be assembled. The outcomes of their pregnancies will be compared with those of three groups of women defined as nonexposed. The comparison cohorts will include:

1. Women resident in the same places as members of the exposed cohort whose pregnancies occurred at times when they could not have been exposed to water during the selected spills.
2. An individually-matched (age, parity, multiple birth and sex of the child) cohort of women resident in Kent and Lambton Counties who were pregnant at the same time as the exposed cohort and were not exposed to water from the St. Clair River.
3. Women resident in Elgin, Huron and Middlesex Counties whose pregnancies occurred at the same time as those of the exposed cohort.

We estimate that a total of 2,000 pregnancies occurred in potentially exposed women in the entire six year period. Investigating only those pregnancies considered to be at risk of exposure to the designated spills will reduce the number to be studied.

The exposure status of the exposed cohort and of nonexposed cohorts 1 and 2 will be confirmed by brief telephone interviews.

Incidence rates of the abnormal outcomes in the exposed cohort will be compared with those of the nonexposed cohorts to evaluate the effects of exposure during the specific spills. Relative risks with 95 per cent confidence limits will be estimated.

PRELIMINARY RESULTS

The preliminary results of the ecologic analyses for the five year period, 1980-1984 are presented in Appendix 2, Tables 1 through 3.3.1. We expect to have the provisional figures for 1985 in the near future. Spontaneous abortions are not included in these tables because data with which to calculate denominators of the rates have only recently become available.

Statistically significant differences in the frequencies of the outcomes of interest were evident only in the exposed group from Kent County. These results are summarized in Tables III and IV. Both stillbirths and perinatal deaths occurred at rates lower than those of the Ontario Southwest Region and the Province as a whole. Since the incidence rate of early neonatal deaths was elevated in the exposed group (Appendix 2, Table 3.1.1), the deficit in stillbirths must account for the deficit in perinatal deaths. The significant increase in low birth weight babies, 1,501 to 2,499 gm., was paralleled by a non-significant increase in babies weighing 1,500 gm. and under (Appendix 2, Table 2.1.1.).

Although they were statistically non-significant certain other observations are worth mentioning. The exposed group in Kent County showed consistently decreased risks of congenital anomalies one of which bordered on significance (Appendix 2, Table 1.2.1). Early neonatal deaths, neonatal deaths and infant deaths all showed consistently high relative risks with upper 95 per cent confidence limits greater than 2 in all but one instance. The major contributor to this appeared to be the early neonatal deaths (Appendix 2, Table 3.1.1.). Since these results are incomplete, we do not believe that they warrant discussion at this time.

Since we have only recently acquired from the Ministry of Health the tape from which we shall draw our control samples for both the case-control and cohort studies, no results are as yet available. We project that the interviewing will start about mid-November, 1986 and that data gathering will be completed by mid-February, 1987. The first draft of the final report will be completed by April 30th, 1987.

Table I.

Abnormal pregnancy and first-year-of-life outcomes chosen for study, Kent and Lambton Counties, 1980-1985.

Outcomes	I.C.D. No.[1]
Pregnancy	
1. Spontaneous abortion	634.0-634.9
2. Stillbirth	-----
3. Live, low birth weight: ≤ 1,500 gm.	
1,501-2,499gm.	765.0
4. Congenital anomalies	
Anencephalus	740.0-740.2
Spina bifida	741.0-741.9
Hydrocephalus	742.3
Congenital heart disease	745.0-747.9
Cleft palate and cleft lip	749.0-749.2
Tracheo-esophageal fistula, esophageal atresia and stenosis	750.3
Atresia and stenosis of large intestine, rectum and anal canal	751.2
Hypospadias and epispadias	752.6
Reduction deformities of upper and lower limbs	755.2-755.4
Down's syndrome	758.0
First-year-of-life	
1. Early neonatal death, 0-6 days	-----
2. Neonatal death, 0-27 days	-----
3. Perinatal death, 0-6 days plus stillbirth	-----
4. Infant death, 0-1 year	-----

---

[1] International Classification of Diseases, 9th Revision, 1979.

Table II.

Selected[1] chemical spills into the St. Clair River, 1980 to 1985.

Year Month Day	Location	Material	Amount metric tons	Recovered Per cent
80-01-08	Sarnia	Bunker C oil	21	38
81-12-21	Sarnia	Bunker C oil	21	81
84-02-22	Sarnia	No. 2 oil	116	80
84-02-27	Sarnia	No. 2 oil	16	81
85-08-13-16	Sarnia	Perchlorethylene	54	100
85-12-19	Sarnia	Isobutylene wash water	26	0

---

[1] Selection was based on: the date of the spill and the material and amount involved.

Table III.

Statistically significant ($P < 0.05$) risks of stillbirth, low birth weight and perinatal death in the exposed group[1], Kent County relative to the Ontario Southwest Region (OSWR)[2] and the Province of Ontario (ON), 1980-1984.

	Comparison areas			
Outcome	OSWR-1	OSWR-2[3]	ON-1	ON-2[3]
Stillbirth				
Risk[4]	0.30	0.30	0.30	0.30
Limits[5]	0.10-0.93	0.10-0.93	0.10-0.93	0.10-0.93
Birth weight 1,501-2,499 gm.				
Risk	1.32	1.32	1.29	1.29
Limits	1.07-1.63	1.07-1.63	1.05-1.59	1.05-1.59
Perinatal Death[6]				
Risk	0.77	0.76	0.78	0.78
Limits	0.63-0.94	0.62-0.92	0.65-0.94	0.65-0.94

[1] Wallaceburg and Tilbury.

[2] The Ontario Southwest Region includes: Bruce, Elgin, Essex, Grey, Huron, Kent, Lambton, Middlesex, Oxford and Perth Counties.

[3] Excluding Kent and Lambton Counties.

[4] Ratios of the incidence rates in the exposed group, Kent County to those of the areas indicated.

[5] 95 per cent confidence limits of the relative risk estimates.

[6] Stillbirths plus deaths 0-6 days.

Table IV.

Statistically significant ($P < 0.05$) risks of stillbirth and low birth weight in the exposed group[1] relative to the nonexposed group, Kent County, 1980-1984.

Outcome	Risk[4]	Limits[5]
Stillbirth	0.28	0.09-0.89
Birth weight 1,501-2,499 gm.	1.30	1.03-1.64

[1,4,5] See Footnotes, Table III.

Appendix 1

REPRODUCTIVE OUTCOMES IN SOUTHWESTERN ONTARIO
1980 to 1985

J. McD. Robertson and H. J. Chan
Dept. of Epidemiology and Biostatistics
The University of Western Ontario

Summary of interview questions

Phase 2 -

1. Identifying data.
2. Time and place of birth of respondent and her parents.
3. Marital status, education, income.
4. Occupation of respondent and spouse.
5. Illnesses, X-rays, ultra sound examinations, prescription and non-prescription medications during the index pregnancy.
6. Cigarette smoking and alcohol, coffee and tea consumption during the index pregnancy.
7. Source of drinking water during the index pregnancy.
8. Consumption of water, drinks reconstituted with water and ice cubes during the index pregnancy.
9. Selected dietary items consumed during the index pregnancy.
10. Use of oral contraceptives prior to the index pregnancy.
11. Outcomes of previous and subsequent pregnancies.
12. Supplementary CONFIDENTIAL questionnaire to be completed by the respondent in private and returned to the interviewer in a sealed envelope.
    - 12.1 Sexually-transmitted diseases prior to the index pregnancy.
    - 12.2 Usual method of contraception prior to the index pregnancy.
    - 12.3 Use of "recreational drugs" during the index pregnancy.

Appendix 2

Table 1.

Total incidence of stillbirth and selected congenital anomalies, Kent and Lambton Counties, the Ontario Southwest Region (OSWR)[1] and the Province of Ontario (ON), 1980-1984.

Area	Total Births	Stillbirths		Congenital anomalies[2]	
	Number	Number	Rate[3]	Number	Rate
Kent County	8,424	56	6.6	48	5.7
Lambton County	9,813	62	6.3	53	5.4
OSWR-1	94,747	659	7.0	491	5.2
OSWR-2[4]	76,510	541	7.1	390	5.1
ON-1	632,972	4,510	7.1	3,371	5.3
ON-2[4]	614,735	4,392	7.1	3,270	5.3

---

[1] The Ontario Southwest Region includes: Bruce, Elgin, Essex, Grey, Huron, Kent, Lambton, Middlesex, Oxford and Perth Counties.

[2] See Table I for a list of diagnoses.

[3] Rate per 1,000 total births.

[4] Excluding Kent and Lambton Counties.

Table 1.1

Relative risks[1] of stillbirth, Kent and Lambton Counties, 1980-1984.

	Stillbirths			
	Kent County		Lambton County	
Comparison area	Risk	Limits[2]	Risk	Limits[2]
OSWR-1	0.94	0.725-1.219	0.90	0.687-1.179
OSWR-2	0.93	0.710-1.218	0.89	0.679-1.166
ON-1	0.93	0.717-1.206	0.89	0.686-1.154
ON-2	0.93	0.717-1.206	0.89	0.686-1.154
Kent vs. Lambton	1.05	0.733-1.505	--	-----

[1] Ratio of the total incidence rates in Kent and Lambton Counties to those of the areas indicated.

[2] 95 per cent confidence limits of the relative risk estimates.

Table 1.1.1.

Total incidence and relative risks[1] of stillbirth in exposed and nonexposed groups, Kent County, 1980-1984.

	Stillbirths - Kent County					
	Exposed[4]			Nonexposed		
Comparison area	Rate[3]	Risk	Limits[2]	Rate	Risk	Limits
	2.1	--	---	7.6	--	---
OSWR-1		0.30*	0.097-0.929		1.09	0.824-1.442
OSWR-2		0.30*	0.097-0.929		1.07	0.809-1.416
ON-1		0.30*	0.097-0.929		1.07	0.817-1.402
ON-2		0.30*	0.097-0.929		1.07	0.817-1.402
Exposed vs. Nonexposed		0.28*	0.088-0.893		--	----
Nonexposed vs. Lambton		1.21	0.836-1.752		--	----

[1,2] See Footnotes, Table 1.1.

[3] See Footnotes, Table 1.

[4] Wallaceburg and Tilbury.

*Significantly different from 1, $P < 0.05$.

Table 1.2.

Relative risks[1] of congenital anomalies, Kent and Lambton Counties, 1980-1984.

	Kent County		Lambton County	
Comparison area	Risk	Limits[2]	Risk	Limits
OSWR-1	1.10	0.815-1.485	1.04	0.786-1.376
OSWR-2	1.12	0.830-1.512	1.06	0.793-1.417
ON-1	1.08	0.816-1.429	1.02	0.779-1.336
ON-2	1.08	0.816-1.429	1.02	0.779-1.336
Kent vs. Lambton	1.06	0.718-1.566	--	-----

[1,2] See Footnotes, Table 1.1.

Table 1.2.1.

Total incidence and relative risks[1] of congenital anomalies in exposed and nonexposed groups, Kent County, 1980-1984.

	Congenital anomalies-Kent County					
	Exposed[4]			Nonexposed		
Comparison area	Rate[3]	Risk	Limits[2]	Rate	Risk	Limits
	3.6	--	---	6.1	--	--
OSWR-1		0.69	0.286-1.664		1.17	0.858-1.595
OSWR-2		0.71	0.294-1.712		1.20	0.880-1.636
ON-1		0.68	0.282-1.639		1.15	0.852-1.552
ON-2		0.68	0.282-1.639		1.15	0.852-1.552
Exposed vs. Nonexposed		0.59	0.235-1.480		--	-----
Exposed vs. Lambton		0.67	0.449-1.000		--	-----

[1-4] See Footnotes, Table 1.1.1.

Table 2.

Live births by birth weight, Kent and Lambton Counties, the Ontario Southwest Region (OSWR)[1] and the Province of Ontario (ON), 1980-1984.

			Live births					
			≤ 1,500gm.		1,501-2,499gm.		≥ 2,500gm.	
Area	Total Number	Unknown Number	Number	Rate[2]	Number	Rate	Number	Rate
Kent County	8,368	0	80	9.6	412	49.2	7,876	941.2
Lambton County	9,751	1	85	8.7	442	45.3	9,223	945.9
OSWR-1	94,088	16	801	8.5	4,341	46.1	88,930	945.2
OSWR-2	75,969	15	636	8.4	3,487	45.9	71,831	945.5
ON-1	628,462	190	5,422	8.6	29,656	47.2	593,194	943.6
ON-2	610,343	189	5,257	8.6	28,802	47.2	576,095	943.9

[1] See Footnote 1, Table 1.

[2] Rate per 1,000 live births.

Table 2.1.

Relative risks[1] of low birth weight, Kent and Lambton Counties, 1980-1984.

	Low birth weight			
	Kent County		Lambton County	
Comparison area	Risk	Limits[2]	Risk	Limits[2]
≤ 1,500gm.				
OSWR-1	1.13	0.898-1.422	1.02	0.819-1.289
OSWR-2	1.14	0.906-1.435	1.04	0.826-1.309
ON-1	1.12	0.899-1.396	1.01	0.819-1.246
ON-2	1.12	0.899-1.396	1.01	0.819-1.246
Kent vs. Lambton	1.10	0.815-1.485	--	-----
1,501 to 2,499gm.				
OSWR-1	1.07	0.978-1.171	0.98	0.887-1.083
OSWR-2	1.07	0.968-1.183	0.99	0.896-1.094
ON-1	1.04	0.941-1.149	0.96	0.877-1.050
ON-2	1.04	0.941-1.149	0.96	0.877-1.050
Kent vs. Lambton	1.09	0.957-1.241	--	-----

[1,2] See Footnotes, Table 1.1.

Table 2.1.1.

Total incidence and relative risks[1] of low birth weight in exposed and nonexposed groups, Kent County, 1980-1984

	Low birth weight - Kent County					
	Exposed[4]			Nonexposed		
Comparison area	Rate[3]	Risk	Limits[2]	Rate	Risk	Limits
≤ 1,500gm.						
	11.4	--	---	9.2	--	---
OSWR-1		1.34	0.821-2.187		1.08	0.841-1.387
OSWR-2		1.36	0.833-2.220		1.09	0.840-1.414
ON-1		1.33	0.815-2.171		1.07	0.833-1.374
ON-2		1.33	0.815-2.171		1.07	0.833-1.374
Exposed vs. Nonexposed		1.24	0.715-2.149		--	-----
Exposed vs. Lambton		1.31	0.771-2.226		--	-----
1,501-2,499gm.						
	60.8	--	---	46.9	--	---
OSWR-1		1.32*	1.070-1.628		1.02	0.914-1.139
OSWR-2		1.32*	1.070-1.628		1.02	0.914-1.139
ON-1		1.29*	1.046-1.591		0.99	0.887-1.105
ON-2		1.29*	1.046-1.591		0.99	0.887-1.105
Exposed vs. Nonexposed		1.30*	1.033-1.636		--	-----
Nonexposed vs. Lambton		1.04	0.904-1.196		--	-----

1,2,4,*See Footnotes, Table 1.1.1.

[3] See Footnote 2, Table 2.

Table 3.

Total incidence of adverse first-year-of-life outcomes, Kent and Lambton Counties, the Ontario Southwest Region (OSWR)[1] and the Province of Ontario (ON), 1980-1984.

Area	Early neonatal deaths[3]		Neonatal deaths[4]		Perinatal deaths[5]		Infant deaths[6]	
	Number	Rate[2]	Number	Rate	Number	Rate	Number	Rate
Kent County	40	4.8	46	5.5	96	11.4	80	9.6
Lambton County	54	5.5	58	5.9	116	11.8	95	9.7
OSWR-1	485	5.1	550	5.8	1,144	12.1	884	9.4
OSWR-2	391	5.1	446	5.9	932	12.2	709	9.3
ON-1	3,026	4.8	3,513	5.6	7,536	11.9	5,312	8.5
ON-2	2,932	4.8	3,409	5.6	7,324	11.9	5,137	8.4

[1] See Footnote 1, Table 1.

[2] Rate per 1,000 live births.

[3] Deaths, 0 to 6 days of age.

[4] Deaths, 0 to 27 days of age.

[5] Stillbirths plus early neonatal deaths.

[6] Deaths, 0 to 1 year of age.

Table 3.1.

Relative risks[1] of neonatal death, Kent and Lambton Counties, 1980-1984.

	Kent County		Lambton County	
Comparison area	Risk	Limits[2]	Risk	Limits[2]
Early neonatal deaths				
OSWR-1	0.94	0.683-1.294	1.08	0.816-1.429
OSWR-2	0.94	0.683-1.294	1.08	0.816-1.429
ON-1	1.00	0.733-1.363	1.15	0.878-1.507
ON-2	1.00	0.733-1.363	1.15	0.878-1.507
Kent vs. Lambton	0.87	0.577-1.311	--	-----
Neonatal deaths				
OSWR-1	0.95	0.704-1.282	1.02	0.779-1.336
OSWR-2	0.93	0.689-1.255	1.00	0.763-1.310
ON-1	0.98	0.733-1.310	1.05	0.810-1.362
ON-2	0.98	0.733-1.310	1.05	0.810-1.362
Kent vs. Lambton	0.93	0.630-1.374	--	-----

[1,2] See Footnotes, Table 1.1

Table 3.1.1

Total incidence and relative risks[1] of neonatal death in exposed and nonexposed groups, Kent County, 1980-1984.

	Neonatal deaths-Kent County					
	Exposed[4]			Nonexposed		
Comparison area	Rate[3]	Risk	Limits[2]	Rate	Risk	Limits
Early neonatal deaths						
	7.1	--	---	4.3	--	---
OSWR-1		1.39	0.748-2.584		0.84	0.580-1.216
OSWR-2		1.39	0.740-2.610		0.84	0.580-1.216
ON-1		1.48	0.796-2.751		0.90	0.628-1.290
ON-2		1.48	0.796-2.751		0.90	0.628-1.290
Exposed vs. Nonexposed		1.65	0.811-3.356		--	-----
Exposed vs. Lambton		1.29	0.660-2.521		--	-----
Neonatal deaths						
	7.1	--	---	5.2	--	---
OSWR-1		1.22	0.656-2.268		0.90	0.641-1.264
OSWR-2		1.20	0.646-2.231		0.88	0.626-1.236
ON-1		1.27	0.683-2.361		0.93	0.669-1.294
ON-2		1.27	0.683-2.361		0.93	0.669-1.294
Exposed vs. Nonexposed		1.37	0.680-2.759		--	-----
Exposed vs. Lambton		1.20	0.614-2.345		--	-----

[1,2,4] See Footnotes, Table 1.1.1.

[3] See Footnote 2, Table 2.

Table 3.2

Relative risks[1] of perinatal death, Kent and Lambton Counties, 1980-1984.

Perinatal Deaths

	Kent County		Lambton County	
Comparison area	Risk	Limits[2]	Risk	Limits
OSWR-1	0.94	0.762-1.160	0.98	0.810-1.190
OSWR-2	0.93	0.754-1.147	0.97	0.802-1.173
ON-1	0.96	0.786-1.173	0.99	0.827-1.185
ON-2	0.96	0.786-1.173	0.99	0.827-1.185
Kent vs. Lambton	0.97	0.740-1.271	--	-----

[1,2] See Footnotes, Table 1.1.

Table 3.2.1

Total incidence and relative risks[1] of perinatal death in exposed and nonexposed groups, Kent County 1980-1984.

	Perinatal deaths-Kent County					
	Exposed[4]			Nonexposed		
Comparison area	Rate[3]	Risk	Limits[2]	Rate	Risk	Limits
	9.3	--	---	11.8	--	---
OSWR-1		0.77*	0.630-0.940		0.98	0.786-1.221
OSWR-2		0.76*	0.622-0.923		0.97	0.778-1.209
ON-1		0.78*	0.645-0.943		0.99	0.794-1.234
ON-2		0.78*	0.645-0.943		0.99	0.794-1.234
Exposed vs. Nonexposed		0.79	0.591-1.056		--	-----
Exposed vs. Lambton		0.79	0.609-1.025		--	-----

[1-4] See Footnotes, Table 1.1.1.

Table 3.3.

Relative risks[1] of infant death, Kent and Lambton Counties, 1980-1984.

Infant Deaths

	Kent County		Lambton County	
Comparison area	Risk	Limits[2]	Risk	Limits
OSWR-1	1.02	0.810-1.284	1.03	0.835-1.271
OSWR-2	1.03	0.818-1.296	1.04	0.843-1.283
ON-1	1.13	0.907-1.408	1.14	0.933-1.392
ON-2	1.14	0.915-1.421	1.15	0.942-1.405
Kent vs. Lambton	0.99	0.733-1.336	--	-----

[1,2] See Footnotes, Table 1.1.

Table 3.3.1

Total incidence and relative risks[1] of infant death in exposed and nonexposed groups, Kent County, 1980-1984.

	Infant deaths-Kent County					
	Exposed[4]			Nonexposed		
Comparison area	Rate[3]	Risk	Limits[2]	Rate	Risk	Limits
	11.4	--	---	9.2	--	---
OSWR-1		1.21	0.741-1.975		0.99	0.771-1.271
OSWR-2		1.23	0.754-2.008		0.99	0.763-1.284
ON-1		1.34	0.812-2.187		1.08	0.841-1.387
ON-2		1.36	0.833-2.220		1.10	0.857-1.412
Exposed vs. Nonexposed		1.24	0.715-2.149		--	-----
Exposed vs. Lambton		1.18	0.695-2.005		--	-----

[1-4] See Footnotes, Table 1.1.1.

Organic Contaminant Structure-Property - Toxicity Relationships for Aquatic Organisms:

A Discussion of Correlations for Narcosis in Aquatic Species

Scott Abernethy

Donald Mackay

Institute for Environmental Studies,

University of Toronto,

Toronto, Ontario

M5S 1A4

ABSTRACT

A hypothesis is presented that narcosis in aquatic organisms occurs when the chemical agent achieves a certain volume fraction (estimated to be 0.63%) in the target phase. If this hypothesis is accepted, it becomes possible to estimate and correlate target-octanol and target-water partition coefficients. Novel methods of presenting QSARs based on these partition coefficients are suggested. The hypothesis is tested on four sets of data totalling 153 determinations of narcosis on fathead minnows, guppies, *Daphnia magna* and *Artemia* with satisfying results. It is suggested that the target-water partitioning characteristics are such that a "cut off" is reached for chemicals in a series of increasing molecular volume, beyond which the chemicals are not able to achieve the required water concentration necessary to establish the volume fraction at the target which causes narcosis.

INTRODUCTION

The mechanism by which a large class of organic chemicals exerts toxic effects on aquatic organisms has been described as a non-specific narcotic or anaesthetic action, with a potency controlled by the organism-water partitioning properties of the chemical. These partitioning properties are in turn controlled by the affinity of the chemical for the water and organic phases, i.e. on activity coefficients or solubilities. A number of QSARs have been developed relating LC50s or EC50s to descriptors such as octanol-water partition coefficient (K_{OW}) or water solubility (eg. Abernethy _et_ _al_., 1985; 1986).

The actual narcotic mechanism remains unclear but it appears that the effect is exerted when a target site accumulates a sufficient volume of chemical to interfere with normal structure and functions. Support for this hypothesis comes from several sources.

In 1939 Ferguson suggested that equal degrees of narcosis were produced when chemicals had similar activities rather than concentrations. Equal activity (expressed as a fraction of chemical solubility) implies equal concentration in phases in which the chemical behaves ideally. If the target site is "ideal" then Ferguson's theory corresponds to approximately equal chemical concentration at the target.

In 1954 Mullins discussed the same principle and introduced a correction for molecular size, the implication being that chemicals of larger molar volume are. more potent because at equal molar concentrations they occupy a larger volume fraction.

Recently Abernethy et al. (1986) have presented and discussed data on LC50s for a variety of chemicals for Daphnia magna and Artemia and have successfully interpreted the results in terms of a postulated constant concentration of toxicant at the target site.

In this paper we discuss this issue further and present an analysis of these data and those of Veith et al. (1983) for fathead minnows and of Könemann (1981) for guppies. The aims are to shed some light on the mechanism of the narcotic effect, identify the relationship between LC50 and K_{OW}, suggest a method of including molar volume as a descriptor and suggest a novel correlation approach. It is emphasized that the thrust is to develop and discuss working hypotheses rather than prove their validity. The data analysis is unconventional, but it is hoped, revealing.

Hypothesis

We hypothesize that when the volume fraction of these chemicals in membranes reaches a critical value, narcosis occurs. Mullins (1954) suggested a figure of 1 to 3% and Carmichael (1985) a figure of approximately 1%. Apparently such "swollen" membranes are unable to function normally and narcosis results. The effect is usually reversible.

Assuming that the entire system of water-organism-target is at equilibrium we can state that the chemical's fugacity (f) in the water (W) and the target (T) site are equal. Applying the conventional (corrected Raoult's Law) equation (Prausnitz, 1969) gives

$$f_W = x_W \gamma_W f_R = f_T = x_T \gamma_T f_R \qquad (1)$$

where x is mole fraction, γ is the activity coefficient and f_R is the reference fugacity or approximately the vapor pressure of the pure liquid chemical. It follows that

$$x_W\gamma_W = x_T\gamma_T \tag{2}$$

The group $x_W\gamma_W$ is the activity as discussed by Ferguson, thus if γ_T is constant for a series of chemicals, equal activity implies equal x_T or equal target site concentration. The volume fraction at the target site y is

$$y = x_Tv_C/\left(x_Tv_C + (1-x_T)v_T\right) \tag{3}$$

where v_C is the molar volume of the chemical, v_T the molar volume of the target site material and $(1 - x_T)$ is the mole fraction of non-toxicant organic material at the target site. Since y for narcosis appears to be of the order of 0.01 it is apparent that x_Tv_C is much smaller than $(1 - x_T)v_T$ and that $(1 - x_T)$ is approximately unity, thus

$$y = x_Tv_C/v_T \tag{4}$$

This definition of y is more equivalent to a volume ratio, than a volume fraction.

Combining equations 2 and 4 gives

$$y = x_W\gamma_Wv_C/(v_T\gamma_T) \tag{5}$$

LC50 concentrations (C_W) are conveniently expressed in mol/m³, or an equivalent unit. Now C_W, is related to mole fraction for dilute solutions as

$$C_W = x_W/v_W \tag{6}$$

where v_W is the molar volume of water (18 x 10⁻⁶ m³/mol).

The term γ_W is the primary determinant of K_{OW}, the relationship being (Miller et al., 1985).

$$K_{OW} = C_O/C_W = x_O v_W/x_W v_O = \gamma_W v_W/\gamma_O v_O \tag{7}$$

where subscript O refers to octanol saturated with water.

Combining equations 6 and 7 with 5 gives

$$y = (C_W K_{OW} v_C)(\gamma_O v_O/\gamma_T v_T) \tag{8}$$

The first group of terms is entirely specific to the chemical and independent of the organism. The second is specific to the chemicals' behaviour in octanol and the target and is actually a target-octanol partition coefficient, which is believed to have a magnitude of appoximately unity, but may vary depending on the nature of the chemical. We designate it as K_{TO} thus

$$y = C_W K_{OW} v_C K_{TO} \tag{9}$$

This equation can be viewed as simply

$$y = C_T v_C \tag{10}$$

where C_T is the target concentration (mol/m³), with C_T being expressed as the product $C_W K_{TW}$, and K_{TW} the target water partition coefficient being further broken down as the product $(K_{OW}\ K_{TO})$.

If y and K_{TO} are constant, experimental values of the group $C_W.K_{OW}.v_C$ or $LC50.K_{OW}.v_C$ should be constant. If that group varies, it is interesting to explore whether the variation is related to variations in K_{OW}, C_W, or v_C. The obvious first step is to examine the magnitude of the group $C_W K_{OW} v_C$ or specifically $LC50.K_{OW}.v_C$.

It transpires that the group is remarkably constant, but contains some variation. We now hypothesize that y is actually constant, and we suggest later a technique for estimating its value. Experimental data are available to estimate the group $(C_W K_{OW} v_C)$. The only remaining variable is K_{TO} which must contain the source of the variation, and which can then be determined and correlated, using an assumed constant value of y and the experimental data.

Data Analyses

QSAR data sets for fathead minnows (Veith *et al.*, 1983), guppies (Könemann, 1981) and *Daphnia* and *Artemia* (Abernethy *et al.*, 1985; 1986) have been analysed as follows.

The LC50 values were ranked in decreasing order for each data set and are listed in Table 1 for the two fish and two crustaceans. Different K_{OW} values for the same compounds between data sets were not adjusted and are shown as given by the original authors. Molar volume was calculated by the Le Bas method (Reid *et al.*, 1977) recognizing that an error of up to a factor of 2 is possible, especially for the smaller molecules. The product of LC50 (mol/m³), K_{OW} and molar volume v_C (cm³/mol), divided by 10^6 to give units of m³/m³, was calculated for each data point. No distinction was made between chemical classes which include alcohols, ketones, ethers, alkanes, cycloalkanes, mono-aromatics, PNAs and a variety of chlorinated hydrocarbons. Nor was a distinction made between test species; all 153 data points being shown as one symbol (n = 42 for fathead minnows, n = 38 for guppies, n = 39 for Daphnia, n = 34 for Artemia). The strength of this data set lies in the number of data points which, it is hoped, is sufficient to enable broad trends to be identified despite differences in QSAR test systems. It is recognized that there are differing sensitivities between species, but if narcosis has a common mechanism, these differences should "average out". Later it may be appropriate to analyse smaller species-specific data sets and obtain more accurate species-specific correlations.

The results are presented in Table 1 and in Figures 1, 2 and 3 in which the ordinate is y/K_{TO} or $(LC50.K_{OW}v_C)$. It is striking that while LC50 and K_{OW} vary over 7 orders of magnitude and v_C by a factor of 3, the group y/K_{TO} varies only from 0.004 to 0.05, a factor of 12.5, for 90% of the chemicals in all four organisms.

There is a tendency for (y/K_{TO}) to increase with increasing K_{OW} and v_C and decrease with LC50. We hypothesize that this is due to a decrease in K_{TO} for substances of lower water solubility and hence higher K_{OW}, usually higher v_C, and lower LC50.

Eleven of the chemicals in Veith's data set, (mostly alcohols and ketones) have log K_{OW} values within the range of zero plus or minus 1.2 units. These chemicals show approximately equal affinities for aqueous and octanol phases and may also (we hypothesize) display equal affinities for the target phase. If this is accepted, K_{TO} for these chemicals is approximately unity thus their mean value of (y/K_{TO}) equals the volume fraction y and is a "true" volume fraction. The mean value is 0.0063, i.e. log y is -2.2. We hypothesize that this is a universal volume fraction and that the variation in (y/K_{TO}) shown in Figures 1, 2 and 3 is entirely due to K_{TO} and, of course, experimental error. This enables us to develop a correlation for K_{TO}.

The log y versus log K_{OW} data were treated by first rejecting about 10% of the "outlying" points then drawing a straight line through the point at which log y is -2.2 and log K_{OW} is 0, such that it split the set of points into two approximately equal groups. The resulting slope on the log-log plot was approximately 0.14. It is thus suggested that

$$K_{TO} = K_{OW}^{-0.14} \tag{11}$$

Examination of the activity coefficient bases for K_{TO} and K_{OW} shows that

$$K_{TO} = (\gamma_O v_O/\gamma_T v_T) = (\gamma_W v_W/\gamma_O v_O)^{-0.14} \tag{12}$$

or

$$\gamma_T v_T = (\gamma_O v_O)^{0.86} (\gamma_W v_W)^{0.14} \tag{13}$$

or

$$\gamma_T \, \alpha \, \gamma_O^{+0.86} \, . \, \gamma_W^{+0.14} \tag{14}$$

Now correlations of K_{OW} versus solubility usually generate slopes of approximately -0.7 to -0.9 which Miller et al. (1985) have interpreted as being the combination of two factors. As γ_W increases (water solubility falls), K_{OW}

increases in proportion (i.e. $\alpha\ \gamma_W^{+1.0}$) but γ_O also increases (i.e. the solubility in octanol falls) with an approximate relationship proportional to $\gamma_W^{0.1}$ to $\gamma_W^{0.3}$ thus the combined effect is a proportionality to the power of 0.7 to 0.9.

A convenient correlation of solubility and K_{OW} which was derived using many of the chemicals considered here is that of Chiou and Schemedding (1982) which is

$$\log K_{OW} = -0.862 \log S + 0.710 \qquad (15)$$

where S is solubility in units of in mol/L. Converting to solubility C_S, or 1000 S mol/m³ gives the algebraically identical forms,

$$\log K_{OW} = -0.862 \log C_S + 3.296 \qquad (16)$$

or

$$K_{OW} = 1977\ C_S^{-0.862} \qquad (17)$$

We interpret this as indicating that, since C_S is inversely proportional to γ_W,

$$K_{OW}\ \alpha\ \gamma_W/\gamma_O\ \alpha\ \gamma_W/(\gamma_W^{0.138})\ \alpha\ \gamma_W^{0.862} \qquad (18)$$

Substituting γ_O as proportional to $\gamma_W^{0.138}$ in equation 13 gives

$$\gamma_T \; \alpha \; \gamma_W^{(0.86 \times 0.138 + 0.14)} \; \alpha \; \gamma_W^{0.26} \qquad (19)$$

The net effect of a decrease in water solubility by a factor of 10, i.e. an increase in γ_W by a factor of 10, is an increase in K_{OW} by a factor of 7.28 (reflecting factors of 10 increase in γ_W and 1.37 in γ_O), a decrease in K_{TO} by a factor of 1.32 caused by factor increases in γ_O of 1.37 and γ_T of 1.82.

The net result is that the target site appears to be more hydrophilic than octanol, i.e. as chemicals increase in hydrophobicity or γ_W, their "solubility" in the target site decreases faster than it does in octanol, i.e. γ_T increases faster than γ_O. It is thus necessary to use a higher concentration in the water to "drive" the chemical into the target site to achieve the required volume fraction of 0.63%.

Figure 4 is a plot of y or 50 $K_{OW}.v_C K_{TO} + 10^6$ or LC50 $K_{OW}^{0.86} v_C + 10^6$, (i.e. assuming K_{TO} is $K_{OW}^{-0.14}$) versus K_{OW}. The constancy around a mean of 0.63% is apparent.

DISCUSSION

Octanol is thus an adequate surrogate for the target site but this analysis suggests that it is a little too hydrophobic. An alcohol such as hexanol could be better. The primary variable which controls the QSAR is clearly γ_W which influences solubility in water directly and thus target-water and octanol-water partitioning. As molecular volume increases in a homologous series, γ_W increases rapidly, γ_T more slowly and γ_O even more slowly.

There are two further noteworthy implications.

First, when correlating LC50s versus molecular properties we suggest that in addition to the conventional log LC50 vs. log K_{OW} plot, the data be examined to test the constancy of the group $LC50.K_{OW}.v_C \div 10^6$. This should have a value of appoximately 0.01. Greater constancy can probably be obtained for a group

$$LC50\ K_{OW}^{(1-n)} v_C \text{ or } LC50.K_{OW}.v_C/K_{OW}^{\ n} \qquad (20)$$

where K_{OW}^{-n} is essentially K_{TO}, the target octanol partition coefficient. We suspect that n will have a value of 0.1 to 0.2. It may also be possible to correlate K_{TO} with variables such as water solubility, γ_W or chemical molar volume. Ultimately, it may be possible to correlate γ_T or more probably the group $\gamma_T v_T$ as a function of molecular properties. If this can be done it becomes possible to avoid using octanol as a surrogate organic phase because

$$y = LC50.K_{OW}.v_C.K_{TO} = LC50.K_{TW}.v_C = LC50.(\gamma_W.v_W/\gamma_T v_T).v_C \qquad (21)$$

The properties of the organism and its target site are entirely described by the group $(\gamma_T v_T)$. Neither v_T or γ_T can be determined individually but their product can be determined, if a constant value of y is assumed. For the data set treated here a typical value of $\gamma_T v_T$ is 1000 cm³/mol.

Second, the equation relating y to LC50 has the interesting property that it predicts a toxicity "cut off", i.e. a point at which the LC50 equals the solubility and at lower solubilities, the chemical can not exert a toxic effect. Graphically, on a plot of log LC50 vs. log solubility, the correlation line crosses the 45° diagonal at low solubility (Abernethy et al., 1986). If we adopt the Chiou-Schmedding correlation between C_S and K_{OW} we can determine the point of cut off as follows

$$\begin{aligned} y &= LC50 \,.\, K_{OW}^{0.86} \,.\, v_C = LC50\,(1977 \,.\, C_S^{-0.862})^{0.86} \,.\, v_C \\ &= 683\,(LC50/C_S) \,.\, C_S^{0.26} \,.\, v_C \end{aligned} \qquad (22)$$

But LC50 equals C_S at the cut off and y is 0.0063 thus

$$\begin{aligned} C_S^{0.26} &= 9.22 \times 10^{-6}/v_C && v_C \text{ in m}^3/\text{mol} \\ &= 9.22/v_C && v_C \text{ in cm}^3/\text{mol} \end{aligned} \qquad (23)$$

or

$$C_S = 9.22^{3.85}/v_C^{3.85} = 5179/v_C^{3.85} \qquad (24)$$

The cut off tends to occur with non polar molecules of v_C approximately

300 cm^3/mol, thus C_S is approximately 1.5 x 10^{-6} mol/m^3 or 4 x 10^{-4} g/m^3 or 0.4 µg/L. Chemicals which have solubilities in the ppb range are thus predicted to lie close to the toxicity cut off. It is interesting that the power on v_C is so large. This corresponds to an apparent rapid fall in toxicity as the cut off is approached. This effect has been previously observed and expressed as a statement that in a series of chemicals,there appears to be a molecular weight or volume cut off beyond which the chemicals become biologically inactive.

This analysis suggests that as molar volume increases in a homologous series, a number of factors combine to give an impression of the rapid onset of biological inactivity. Typically a 10% or factor 1.1 increase in v_C eg. approximately from 285 to 315 cm^3/mol causes

(i) an increase in γ_W (and a corresponding decrease in water solubility) by a factor of 5 (Miller et al., 1985),

(ii) an increase in γ_T (and a corresponding decrease in "solubility" at the target by a factor of $5^{0.26}$ or 1.52.

(iii) an increase in volume occupied per molecule by a fraction of 1.1.

The last two factors combined decrease the ability of the chemical to occupy volume in the target by a factor of 1.52/1.1 or 1.38, necessitating an increase in water concentration by this factor to compensate for the loss of affinity to the target. A lower water concentration is needed to exert the toxic effect by a factor of 5/1.38 of 3.6. But since the solubility of the chemical is inversely proportional to γ_W, this solubility has fallen by a factor of 5. The required LC50 concentration thus moves closer to the solubility as both fall. Eventually, the required water concentration or LC50 reaches the solubility limit and a cut off occurs. The approach to the cut off is very non-linear, a 10% increase in molar volume necessitating a 38% increase in activity or ratio of water concentration to solubility.

Another factor which may also contribute to an even more rapid cut off is the onset of chemical solidification, i.e when the melting point is reached. All the solubilities discussed here are liquid or subcooled liquid solubilities. As molecular weight and volume increase the melting point falls and approaches the test temperature. Below the melting point the chemical cannot form solutions as concentrated as the subcooled liquid value since it is constrained to a lower solid solubility by virtue of the accessibility of a lower energy crystalline form.

CONCLUSIONS

This analyses of narcosis data for a variety of chemicals for four aquatic organisms suggests that simple log LC50 vs. log K_{OW} correlations should be regarded as only a first step in interpretation. It appears that narcosis occurs at a fairly constant volume fraction increase in the target site of approximately 0.63%. The factors contributing to this level of partitioning have been discussed and it is postulated that the target-water partition coefficient differs from the octanol-water partition coefficient. As a series of chemicals increases in molar volume or hydrophobicity, their "solubility" in the target phase tends to decrease, i.e. the activity coefficient increases, until a point is reached at which the water concentration required to drive the toxicant into the target phase to achieve the required volume fraction equals the water solubility. Beyond this point, chemicals appear to be biologically inactive.

An obvious next stage is to treat each species separately and quantify differences in species sensitivities in terms of specific target-water or target-octanol partition coefficients. But it would be useful if the correlation techniques were identical such that inter-species comparisons can be made more easily.

It is hoped that this discussion will encourage other innovative correlation and interpretation approaches and thus contribute to a fuller understanding of the fundamental biology and chemistry underlying QSARs.

REFERENCES

Abernethy, S., Charles, C., Mackay D. 1985. Development of predictive organic contaminant structure-property-toxicity relationships for aquatic organisms, p 333-356 In Proceedings of the Technology Transfer Conference, Toronto, Dec. 1985. Ontario Ministry of the Environment.

Abernethy, S., Bobra, A.M., Shiu, W.Y., Wells, P.G., Mackay, D. 1986. Acute lethal toxicity of hydrocarbons and chlorinated hydrocarbons to two planktonic crustaceans: the key role of organism-water partitioning. Aq. Toxicol. 8:163-174.

Carmichael, F.J. 1985. General anaesthetics. p.265-289. H. Kalant et al. [Eds.] Principles of Medical Pharmacology, University of Toronto Press, Toronto.

Chiou, C.T., Schmedding, D.W., Manes, M. 1982. Partitioning of organic compounds in octanol-water systems. Environ. Sci. Technol. J. 16:4-10.

Ferguson, J. 1939. Use of chemical potentials as indices of toxicity. Proc. R. Soc. Lond. Ser. B. 127:387-404.

Könemann, H. 1981. Quantitative structure-activity relationships in fish toxicity studies. Toxicol. 19:209-221.

Miller, M., Wasik, S.P., Huang, G.L., Shiu, W.Y., Mackay, D. 1985. Relationships between octanol-water partition coefficient and aqueous solubility. Environ. Sci. and Technol. J. 6:522-529.

Mullins, L.J. 1954. Some physical mechanisms in narcosis. Chem. Rev. 54:289-323.

Prausnitz, J.M. 1969. Molecular thermodynamics of fluid-phase equilibria, Prentice Hall, New Jersey.

Reid, R.C., Prausnitz, J.M., Sherwood, T.K. 1977. The properties of gases and liquids, 3rd ed., p.58. McGraw-Hill, New York.

Veith, R.C., Call, D.J., Brook, L.T. 1983. Structure-toxicity relationships for the fathead minnow. Can. J. Fish Aq. Sci. 40:743-748.

Table 1:Toxicological and physical-chemical data used to calculate volume fraction for non-specific effects on fish and crustaceans.

COMPOUND (data source) (Veith,et al.,1983)	y/K TO	LOG LC50 (mol/m^3)	LOG Kow	MOLAR VOLUME (cm^3/mol)
Triethylene glycol	0.0057	2.67	-1.17	180.00
Acetone	0.0060	2.15	-0.24	74.00
2-Methyl-2.4-pentanediol	0.0028	1.96	-0.70	155.00
2-Butanone	0.0082	1.65	0.28	96.00
Tetrahydrofuran	0.0071	1.48	0.46	81.00
2-Methyl-1-propanol	0.0096	1.28	0.74	92.00
3-Pentanone	0.0145	1.25	0.84	118.00
3-Methyl-2-butanone	0.0049	1.00	0.62	118.00
t-Butylmethyl ether	0.0204	0.90	1.30	129.00
Cyclohexanol	0.0147	0.85	1.23	122.00
Cyclohexanone	0.0041	0.73	0.81	118.00
4-Methyl-2-pentanone	0.0126	0.70	1.25	141.00
2-Phenoxyethanol	0.0056	0.40	1.16	155.00
2,2,2-Trichloroethanol	0.0058	0.30	1.38	122.00
5-Methyl-2-hexanone	0.0139	0.14	1.79	163.00
Acetophenone	0.0086	0.13	1.66	140.00
1,2-Dichloroethane	0.0069	0.08	1.79	93.00
Diisopropyl ether	0.0049	-0.05	1.56	152.00
3,3-Dimethyl-2-butanone	0.0011	-0.06	0.94	141.00
1,1.2-Trichloroethane	0.0083	-0.21	2.07	115.00
1,1,2-Trichloroethylene	0.0095	-0.47	2.42	107.00
2-Hydroxy-4-methoxyacetophenone	0.0081	-0.48	2.14	177.00
Di-n-butyl ether	0.0592	-0.60	3.08	196.00
5-Nonanone	0.0453	-0.66	3.00	207.00
2-Octanone	0.0117	-0.66	2.46	185.00
1-Fluoro-4-nitrobenzene	0.0027	-0.70	2.02	127.00
2,6-Dimethoxytoluene	0.0121	-0.87	2.67	192.00
1,1,2,2-Tetrachloroethane	0.0166	-0.92	3.01	135.00
Benzophenone	0.0413	-1.08	3.38	207.00
Tetrachloroethylene	0.0035	-1.09	2.53	128.00
2,4-Dichloroacetophenone	0.0118	-1.21	3.02	182.00
1,3-Dichlorobenzene	0.0174	-1.28	3.38	138.00
2-Decanone	0.0290	-1.44	3.54	230.00
Pentachloroethane	0.0247	-1.44	3.64	156.00
1,4-Dichlorobenzene	0.0089	-1.56	3.37	138.00
Dipentyl ether	0.0663	-1.70	4.16	230.00
3,4-Dichlorotoluene	0.0528	-1.74	4.22	175.00
1,2,4-Trichlorobenzene	0.0480	-1.80	4.28	159.00
2,3,4-Trichloroacetophenone	0.0097	-2.05	3.73	203.00
Hexachloroethane	0.0466	-2.20	4.62	177.00
1,2,3,4-Tetrachlorobenzene	0.0897	-2.29	4.99	179.00
α,α-2,6-tetrachlorotoluene	0.0157	-2.38	4.24	217.00

(Konemann,1981)	y/K_{TO}	LOG $LC50$ (mol/m^3)	LOG Kow	MOLAR VOLUME (cm^3/mol)
Acetone	0.0041	2.04	-0.30	74.00
Diethylether	0.0201	1.46	0.88	92.00
Dichloromethane	0.0080	0.54	1.51	71.00
1,1-Dichloroethane	0.0160	0.31	1.92	94.00
1,2-Dichloroethane	0.0058	0.03	1.76	94.00
1-Chlorobutane	0.0274	0.02	2.35	117.00
1,2-Dichloropropane	0.0172	0.01	2.16	116.00
1,1,1-Trichloroethane	0.0355	0.00	2.49	115.00
Chloroform	0.0082	-0.07	2.02	92.00
Benzene	0.0105	-0.09	2.13	96.00
Toluene	0.0340	-0.13	2.59	118.00
1,3-Dichloropropane	0.0044	-0.13	1.71	116.00
1,1,2-Trichloroethane	0.0195	-0.15	2.38	115.00
Tetrachloromethane	0.0318	-0.34	2.79	113.00
Trichloroethane	0.0076	-0.38	2.20	115.00
m-Xylene	0.0611	-0.45	3.09	140.00
o-Xylene	0.0570	-0.48	3.09	140.00
p-Xylene	0.0570	-0.48	3.09	140.00
1,2,3-Trichloropropane	0.0165	-0.55	2.63	137.00
1,1,2,2-Tetrachloroethane	0.0302	-0.66	3.01	135.00
Monochlorobenzene	0.0128	-0.77	2.81	117.00
3-Chlorotoluene	0.0410	-0.84	3.31	139.00
Tetrachloroethane	0.0129	-0.97	2.95	135.00
Pentachloroethane	0.0440	-1.13	3.58	156.00
1,3-Dichlorobenzene	0.0234	-1.30	3.53	138.00
4-Chlorotoluene	0.0133	-1.33	3.31	139.00
1,2-Dichlorobenzene	0.0186	-1.40	3.53	138.00
3,4-Dichlorotoluene	0.0528	-1.50	3.98	175.00
2,4-Dichlorotoluene	0.0482	-1.54	3.98	175.00
1,4-Dichlorobenzene	0.0126	-1.57	3.53	138.00
1,3,5-Trichlorobenzene	0.0459	-1.74	4.20	159.00
1,2,4-Trichlorobenzene	0.0332	-1.88	4.20	159.00
1,2,3-Trichlorobenzene	0.0325	-1.89	4.20	159.00
2,4,5-Trichlorotoluene	0.0827	-2.06	4.72	181.00
1,2,3,4-Tetrachlorobenzene	0.0579	-2.43	4.94	179.00
1,2,3,5-Tetrachlorobenzene	0.0579	-2.43	4.94	179.00
1,2,4,5-Tetrachlorobenzene	0.0220	-2.85	4.94	179.00
Pentachlorobenzene	0.0693	-3.15	5.69	200.00

(Abernethy,et al.,1986)	y/K_{TO}	LOG LC50 (mol/m^3)	LOG Kow	MOLAR VOLUME (cm^3/mol)
Dichloromethane	0.0037	0.20	1.51	71.00
Trichloromethane	0.0064	-0.18	2.02	92.00
1,1,1-Trichloroethane	0.0153	-0.37	2.49	115.00
Benzene	0.0052	-0.40	2.13	96.00
Carbon tetrachloride	0.0127	-0.74	2.79	113.00
Cyclopentane	0.0150	-0.82	3.00	100.00
Pentane	0.0312	-0.87	3.30	116.00
Toluene	0.0057	-0.90	2.59	118.00
m-Xylene	0.0154	-1.05	3.09	140.00
p-Xylene	0.0137	-1.10	3.09	140.00
Trichloroethylene	0.0017	-1.23	2.42	107.00
Chlorobenzene	0.0038	-1.29	2.80	117.00
1,3,5-Trimethylbenzene	0.0290	-1.30	3.55	163.00
Hexane	0.0369	-1.35	3.80	131.00
Cyclohexane	0.0145	-1.35	3.44	118.00
Naphthalene	0.0214	-1.43	3.59	148.00
1,3-Dichlorobenzene	0.0115	-1.48	3.40	138.00
o-Xylene	0.0052	-1.52	3.09	140.00
1,2,4-Trimethylbenzene	0.0175	-1.52	3.55	163.00
1,4-Dichlorobenzene	0.0083	-1.62	3.40	138.00
Ethylbenzene	0.0038	-1.70	3.13	140.00
1,2,4-Trichlorobenzene	0.0356	-1.75	4.10	159.00
1,2-Dichlorobenzene	0.0055	-1.80	3.40	138.00
Methyl cyclohexane	0.0154	-1.82	3.86	140.00
2-Methylnaphthalene	0.0132	-1.98	3.87	170.00
2-Chloronaphthalene	0.0173	-2.00	4.08	144.00
1-Methylnaphthalene	0.0126	-2.00	3.87	170.00
1,3,5-Trichlorobenzene	0.0174	-2.06	4.10	159.00
1,2,3-Trichlorobenzene	0.0159	-2.10	4.10	159.00
Biphenyl	0.0104	-2.15	3.90	185.00
1,2,3,4-Tetrachlorobenzene	0.0285	-2.30	4.50	180.00
1,2,3,5-tetrachlorobenzene	0.0227	-2.40	4.50	180.00
1,2,4,5-Tetramethylbenzene	0.0072	-2.46	4.05	185.00
Octane	0.0431	-2.48	4.90	164.00
Pentachlorobenzene	0.0240	-2.92	5.00	200.00
Phenanthrene	0.0066	-2.94	4.46	199.00
9-Methylanthracene	0.0186	-3.19	5.12	219.00
Pyrene	0.0076	-3.35	4.90	214.00
Decane	0.0229	-3.70	5.70	229.00

(Abernethy,et al.,1986)	y/K_{TO}	LOG LC50 (mol/m^3)	LOG Kow	MOLAR VOLUME (cm^3/mol)
Dichloromethane	0.0138	0.78	1.51	71.00
Benzene	0.0210	0.21	2.13	96.00
Trichloromethane	0.0139	0.16	2.02	92.00
Toluene	0.0296	-0.19	2.59	118.00
Chlorobenzene	0.0268	-0.44	2.80	117.00
Cyclopentane	0.0282	-0.55	3.00	100.00
p-Xylene	0.0395	-0.64	3.09	140.00
o-Xylene	0.0386	-0.65	3.09	140.00
Carbon tetrachloride	0.0139	-0.70	2.79	113.00
m-Xylene	0.0313	-0.74	3.09	140.00
Pentane	0.0381	-0.78	3.30	116.00
Ethylbenzene	0.0273	-0.84	3.13	140.00
1,3,5-Trimethylbenzene	0.0679	-0.93	3.55	163.00
Cumene	0.0541	-0.94	3.50	149.00
1,2-Dichlorobenzene	0.0355	-0.99	3.40	138.00
1,2,4-Trimethylbenzene	0.0578	-1.00	3.55	163.00
1,4-Dichlorobenzene	0.0324	-1.03	3.40	138.00
Cyclohexane	0.0277	-1.07	3.44	118.00
Naphthalene	0.0479	-1.08	3.59	148.00
1,3-Dichlorobenzene	0.0263	-1.12	3.40	138.00
Hexane	0.0337	-1.39	3.80	131.00
Methyl cyclohexane	0.0377	-1.43	3.86	140.00
2-Methylnaphthalene	0.0417	-1.48	3.87	170.00
Biphenyl	0.0378	-1.59	3.90	185.00
1-Methylnaphthalene	0.0224	-1.75	3.87	170.00
1,2,4-Trichlorobenzene	0.0356	-1.75	4.10	159.00
2-Chloronaphthalene	0.0245	-1.85	4.08	144.00
1,2,3-Trichlorobenzene	0.0258	-1.89	4.10	159.00
1-Chloronaphthalene	0.0194	-1.95	4.08	144.00
1,2,3,5-Tetrachlorobenzene	0.0422	-2.13	4.50	180.00
1,3,5-Trichlorobenzene	0.0105	-2.28	4.10	159.00
1,2,3,4-Tetrachlorobenzene	0.0285	-2.30	4.50	180.00
Phenanthrene	0.0218	-2.42	4.46	199.00
Octane	0.0452	-2.46	4.90	164.00

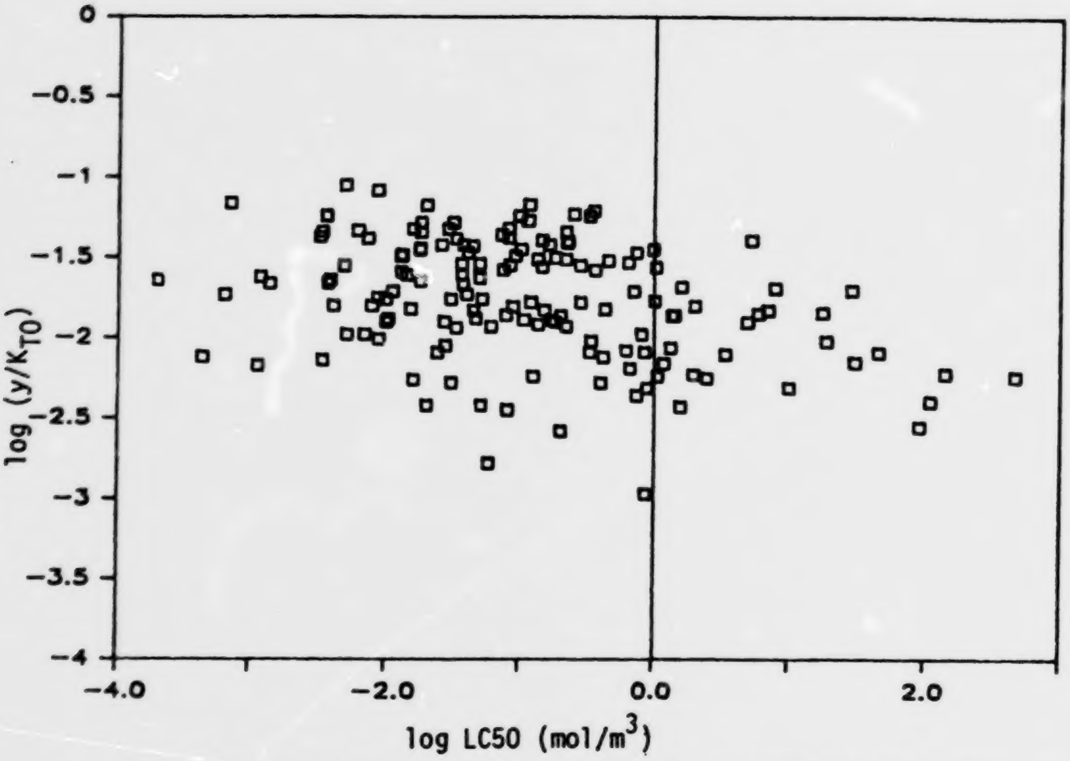


Figure 1:Variation in volume fraction as a function of median lethal concentration.

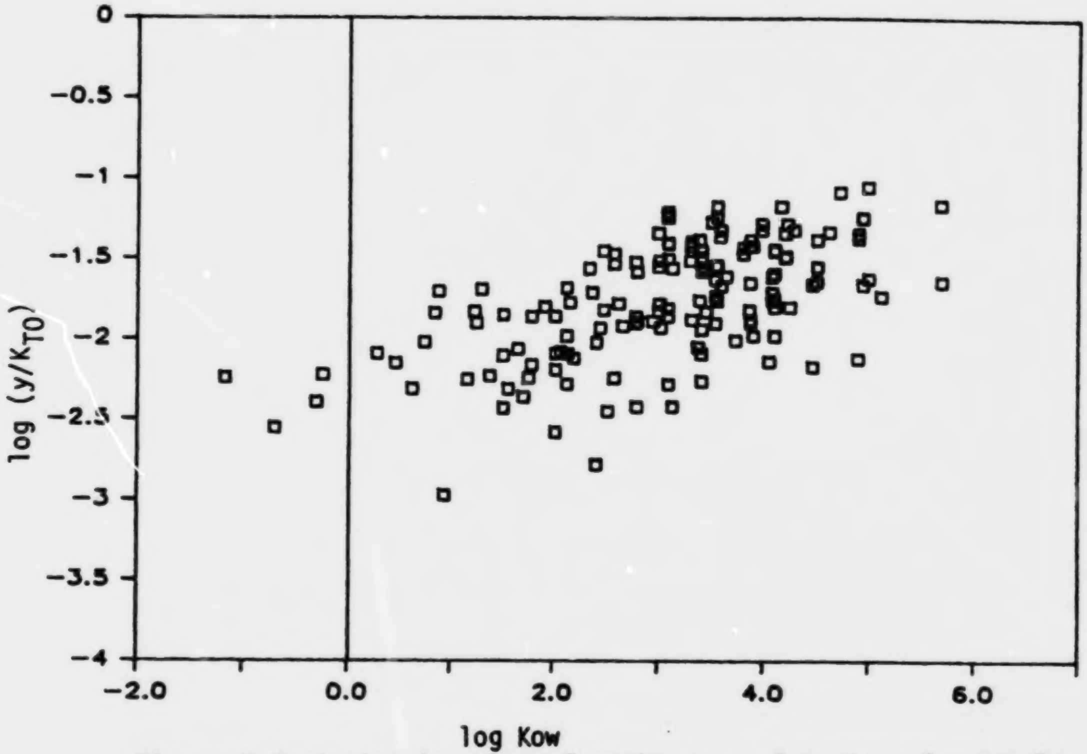


Figure 2:Variation in volume fraction as a function of octanol-water partition coefficient.

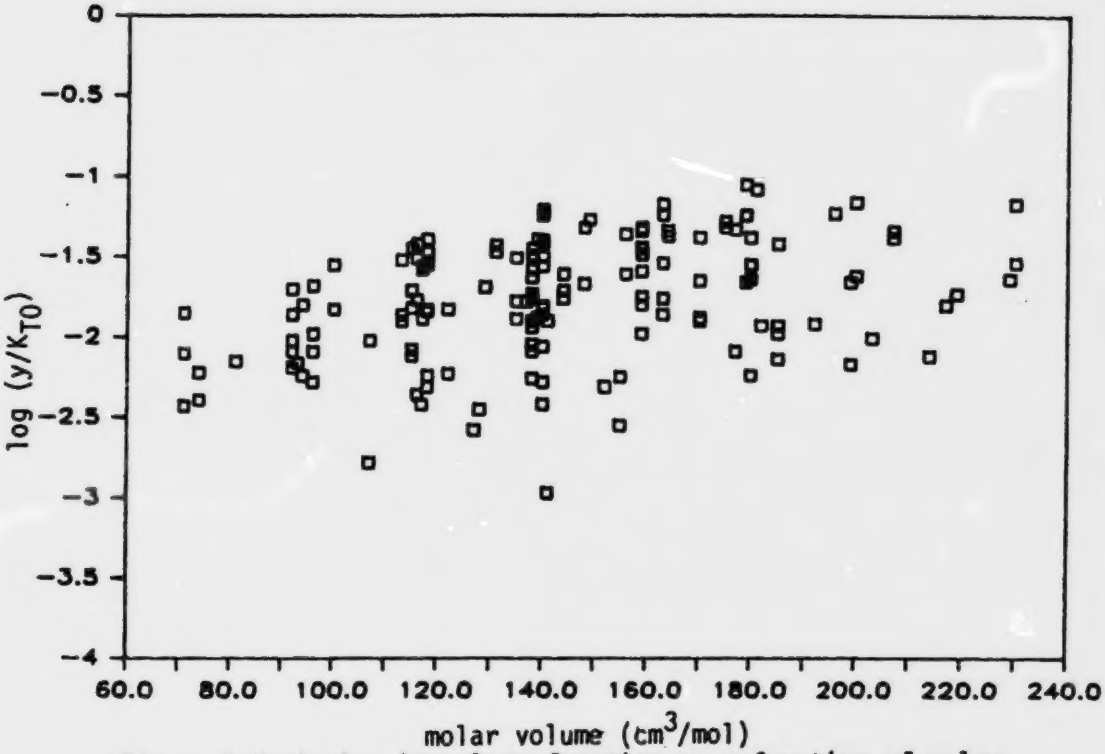


Figure 3:Variation in volume fraction as a function of molar volume.

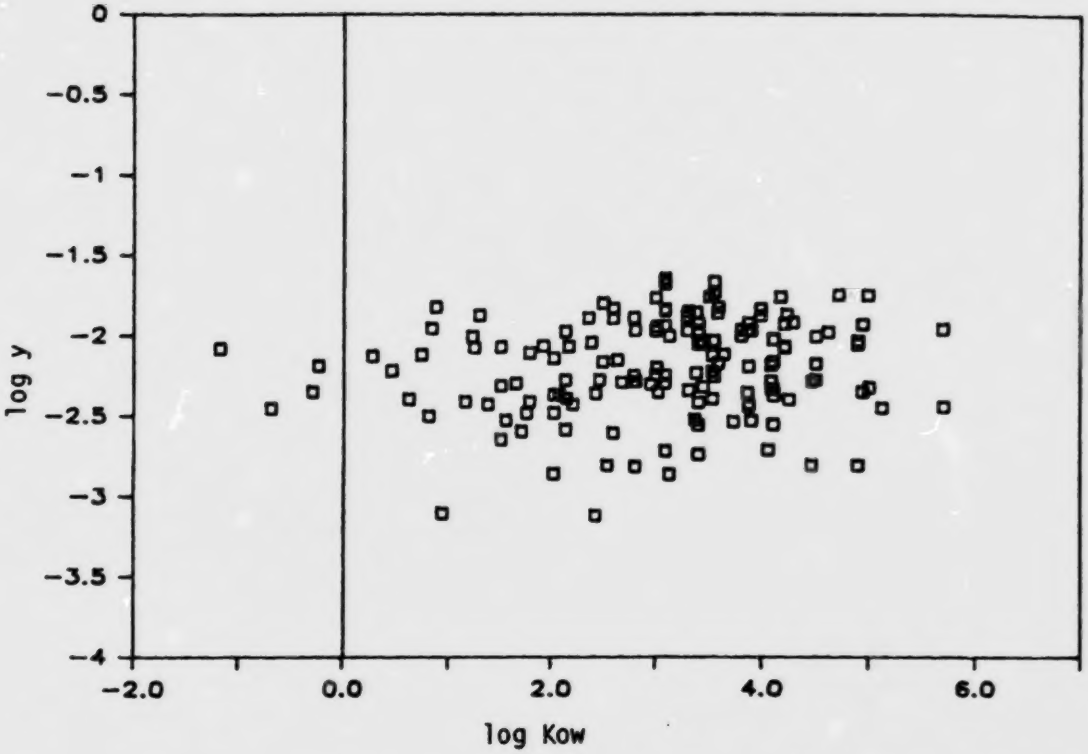


Figure 4: Variation in y, $(LC50*Kow^{0.86}*v_c \div 10^6)$ as a function of octanol-water partition coefficient.

EFFECT OF EXPOSURE TO LEAD, CADMIUM AND MERCURY ON THE TISSUE OF FISH AND RATS: DEVELOPMENT OF A BIOINDICATOR

NICHOLLS, D.M., Angelow, R. and Teichert-Kuliszewska, K.,
Department of Biology, York University,
North York, Ont. M3J 1P3

and

Girgis, G.R.,
Department of Applied Chemistry, Seneca College,
Finch Avenue, Willowdale, North York, Ont. M2J 2X5.

INTRODUCTION

There is considerable recent work which suggests that blood and tissue levels of environmental pollutants, such as the heavy metals, are not correlated with the functional impairment of the animal. Since protein synthesis is the broadest possible measure of overall animal health, it is surprising how few measurements have been carried out in animals growing in "healthy" environments,[20,21] let alone in environments polluted with cadmium, lead, and mercury. Protein synthesis in specific target tissues, such as muscle, liver, kidney and brain, have been studied in rats and more recently in fish in our laboratory.[7] The results indicate considerable pathology as the concentration of pollutant and time of exposure are increased.

In addition to studying the complex machinery of protein synthesis in these animals, we have focussed on simplifying the methodology by measuring the most crucial elements, namely mRNA and elongation enzymes.[8-11]

Furthermore, there are several reports of heavy metal effects on several key metabolic enzymes of glycolysis and amino acid metabolism in fish exposed to relatively high levels of lead or cadmium.[12-15] Thus, we have carried out a broad range of experiments in the laboratory on goldfish and field-collected yellow perch to examine some of these key metabolic enzymes, and additionally membrane enzymes, since membranes are thought to be the primary site, for example, of mercury and methylmercury effects.

METHODS

Animals

Fish were 2-4 inches in size throughout the experiments. Goldfish (Carassius auratus) were exposed to dechlorinated Toronto tap water, acidified to pH 5.0 ,containing 5, 100 or 500 μg Pb/1 as Pb acetate in a static bioassay for periods of 3, 6 or 20 weeks. The water (15 l) was acidified with an appropriate volume of H_2SO_4 added to the aquaria. In a subsequent series the acidified water contained 25 μg Pb/l in combination with 0.25 μg Cd/l and 0.25 μg Hg/l for 3 or 6 weeks. The next experiment used acidified water containing only Hg 30 μg/l for 3 weeks or 6 weeks. The fish were fed daily on fish pellets.

The aquaria were in a room at 17 ± 1°C. The control water and metal-containing water were replaced weekly. In an experiment using 30 μg/l, the level of Hg detected in the water of the aquaria on the seventh day had fallen to approximately 1.5 μg/l. Normally each aquarium (15 l) contained no more than 10 fish.

A new series of experiments is studying rainbow trout (Salmo gairdneri) exposed in a flow bioassay system to Hg at concentrations of 0.2, 0.5, 1.0 and 5.0 μg/l for up to 2 weeks. Yellow perch from impacted and clean Muskoka lakes have been studied as well, either 1 or 2 days after collection.

Chemicals:

H_2SO_4, $HgCl_2$, $CdCl_2 \cdot 2.5\ H_2O$ and $Pb(C_2H_3O_2) \cdot 3H_2O$ were from Fisher Scientific Co., Don Mills, Ontario, and were of certified ACS grade. Other chemicals were obtained as described previously.

The components of the enzyme assays were obtained from Sigma Chemical Co., St. Louis, MO. U.S.A. L-[U-^{14}C] leucine (339 Ci/mol) was from Amersham Corp., Oakville, Ontario.

Enzyme Assays:

Glyceraldehyde-3-phosphate dehydrogenase (GAPDH) EC 1.2.1.12 was assayed as described by Patnode *et al*. (1976)[2]. Lactate dehydrogenase (LDH, EC 1.1.1.27) was assayed as described by Kornberg (1955)[3] and aldolase (ALD, EC 4.1.2.13) was measured using a reagent kit obtained from the Sigma Chemical Co., St. Louis, MO, USA. Pyruvate kinase (PK, EC 2.7.1.40) was assayed as described by Bucher and Pfleiderer (1955)[3a]. The method of Glossman and Neville (1972)[4] was used to assay γ-glutamyltranspeptidase (EC 2.3.2.2) while alanine aminopeptidase was assayed by the method of Pfleiderer (1970)[5]. Alkaline phosphatase (EC 3.1.3.1) was as described by Quirk and Robinson (1972)[6].

Preparation of tissue homogenates:

For muscle, the tissue was treated for 30 s in a mixer (model SDT: Tekmar, Cincinnati, OH, USA) before the homogenization step, while liver was homogenized directly. The tissues were homogenized in a glass homogenizer with 12-15 passes of a Teflon pestle in 1 mM EDTA and 1 mM 2-mercaptoethanol, pH 7.0, and centrifuged at 3000 x g for 20 min at 4°C as described by Patnode *et al*. (1976)[2]. The resultant supernatant fluid was centrifuged at 10,000 x g for 20 min and the resultant clear supernatant fluid was frozen at -20°C or used immediately for determining the enzyme activities.

Protein synthesis:

Muscle and liver were homogenized as above in 3 volumes of buffer containing 0.25 M sucrose, 50 mM Tris.HCl (pH 7.8 at 24°C), 80 mM potassium acetate, 5 mM magnesium acetate, and 10 mM 2-mercaptoethanol. Centrifugation at 4°C at 15,000 g for 15 min and 105,000 g for 70 min to sediment the mitochondrial and microsomal fractions, respectively, yielded the postmicrosomal supernatant fraction (S105) as described by Sauvé and Nicholls (1981)[9]. The S105 fraction contained the enzymes of protein synthesis which were incubated with rat liver ribosomes as described by Sauvé and Nicholls (1981)[9]. The incorporation of $[^{14}C]$ leucine into protein was measured following termination of the incubation with 10% trichloroacetic acid and washing of the protein with hot 5% trichloroacetic acid. Solubilization of the protein for liquid scintillation counting was described previously (Sauvé and Nicholls, 1981)[9]. In other experiments ribosomes bearing mRNA were obtained from the microsomal fraction and were incubated with S105 supernatant fraction from rat liver (as a source of synthetases and elongation factors) as we described previously.[10]

Miscellaneous:

Protein concentration was determined according to the method of Lowry et al. (1951)[7] using 1% bovine serum albumin as a standard. The RNA concentration was determined by the absorbance at 260 mm using A 1.0 = 50 g/ml. The absorbances were measured on a Zeiss model PMQII spectrophotometer. Values reported are mean ± SE. P-values by Student's t-test that are <0.05 are underlined.

TABLE 1

The activity of enzymes of glycolysis and of membranes in fish tissue following exposure to lead for 3 weeks

	DOSE (μg/1)	Enzyme Activity (μmoles/mg protein/hr) LIVER Control	LIVER Lead	MUSCLE Control	MUSCLE Lead
Glyceraldehyde-3-phosphate dehydrogenase	500	12.6 ± 1.2	13.2 ± 0.6	11.4 ± 0.6	6.6 ± 0.6
	100	12.6 ± 0.6	15.6 ± 1.8	10.2 ± 0.6	7.2 ± 0.6
Lactate dehydrogenase	500	49.2 ± 3.6	96.0 ± 6.6	58.8 ± 6.0	60.0 ± 6.0
	100	48.0 ± 3.6	82.2 ± 9.0	57.6 ± 10.8	56.4 ± 3.6
γ-glutamyl transpeptidase	500	1.80 ± 0.04	2.30 ± 0.06		
	100	1.82 ± 0.12	2.40 ± 0.30		
Aminopeptidase	500	4.52 ± 0.42	7.10 ± 0.44		
	100	2.50 ± 0.10	3.50 ± 0.05		

Mean ± S.D. for 2 experiments, each of 3-4 fish

TABLE 2

The activity of enzymes of glycolysis and of membranes in fish tissue following exposure to lead for 6 weeks

	DOSE (µg/1)	Enzyme Activity (µmoles/mg protein/hr) LIVER Control	LIVER Lead	MUSCLE Control	MUSCLE Lead
Glyceraldehyde-3-phosphate dehydrogenase	500	11.4 ± 0.6	13.2 ± 1.2	10.8 ± 1.2	6.6 ± 0.6
	100	12.0 ± 1.2	14.4 ± 1.2	10.2 ± 0.6	8.4 ± 0.6
Lactate dehydrogenase	500	54.6 ± 1.2	115.2 ± 12	60.0 ± 4.8	66.6 ± 4.8
	100	51.6 ± 7.8	88.2 ± 11	50.0 ± 7.8	54.0 ± 8.4
γ-glutamyl transpeptidase	500	1.60 ± 0.07	2.46 ± 0.36		
	100	1.49 ± 0.27	1.81 ± 0.26		
Aminopeptidase	500	3.65 ± 0.20	7.78 ± 0.15		
	100	4.17 ± 0.27	6.25 ± 0.41		

Mean ± S.D. for 2 experiments, each of 3-4 fish

Table 3

The activity of enzymes of glycolysis and of membranes in fish tissue following exposure to low levels of mercury, cadmium and lead for 3 weeks.

Glycolytic Enzyme Activity
(μmoles/mg protein/hr)

	LIVER		MUSCLE	
	Control	Heavy Metals	Control	Heavy Metals
Glyceraldehyde-3-phosphate dehydrogenase	13.2 ± 0.42	11.4 ± 0.42	16.8 ± 0.60	10.2 ± 0.62
Lactate dehydrogenase	38.4 ± 3.6	45.0 ± 6.0	46.2 + 5.4	20.4 ± 0.60
Aldolase	7.60 ± 0.24	7.22 ± 0.90	44.0 ± 3.0	40.7 + 1.7
Pyruvic kinase	63.5 ± 2.3	61.4 ± 0.89	98.3 ± 6.6	100 ± 4.3

Membrane Enzyme Activity
(μmoles/mg protein/hr)

	LIVER		MUSCLE	
	Control	Heavy Metals	Control	Heavy Metals
γ-glutamyl transpeptidase	1.48 ± 0.06	1.61 ± 0.07	0.89 ± 0.17	0.67 ± 0.16
Aminopeptidase	3.61 ± 0.30	3.66 ± 0.35	1.22 ± 0.11	1.14 ± 0.05
Alkaline phosphatase	7.89 ± 0.55	10.1 ± 0.34	11.8 ± 0.46	9.83 ± 1.06

Mean ± SEM for 3 experiments of 6 fish.

Table 4

The activity of enzymes of glycolysis and of membranes in fish tissue following exposure to low levels of mercury, cadmium and lead for 6 weeks.

Glycolytic Enzyme Activity (μmoles/mg protein/hr)

	LIVER		MUSCLE	
	Control	Heavy Metals	Control	Heavy Metals
Glyceraldehyde-3-phosphate dehydrogenase	11.6 ± 0.72	10.9 ± 0.60	12.6 ± 0.60	9.36 ± 0.48
Lactate dehydrogenase	59.2 ± 2.88	61.8 ± 3.12	68.4 ± 3.96	51.9 ± 1.50
Aldolase	8.97 ± 0.34	8.31 ± 0.22	40.4 ± 2.13	43.0 ± 1.58
Pyruvic kinase	62.8 ± 1.86	60.0 ± 0.65	96.3 ± 4.85	99.2 ± 4.24

Membrane Enzyme Activity (μmoles/mg protein/hr)

	LIVER		MUSCLE	
	Control	Heavy Metals	Control	Heavy Metals
γ-glutamyl transpeptidase	1.61 ± 0.12	1.84 ± 0.05	1.04 ± 0.09	1.11 ± 0.08
Aminopeptidase	3.17 ± 0.09	3.27 ± 0.19	1.82 ± 0.21	1.56 ± 0.09
Alkaline phosphatase	7.59 ± 0.81	13.9 ± 0.58	12.6 ± 0.13	10.0 ± 0.10

Mean ± SEM for 3 experiments of 6 fish.

TABLE 5

The activity of enzymes of glycolysis and of membranes in fish tissues following exposure to mercury (30 μg/1) for 3 weeks

	Enzyme Activity (μmoles/mg protein/hr)			
	LIVER		MUSCLE	
	Control	Mercury	Control	Mercury
Glyceraldehyde-3-phosphate dehydrogenase	10.2 ± 0.6	7.8 ± 0.6	15.0 ± 0.6	10.2 ± 0.6
Lactate dehydrogenase	53.4 ± 1.2	43.2 ± 3.6	42.0 ± 2.4	37.8 ± 3.0
Aldolase	8.91 ± 0.60	8.80 ± 0.53	46.0 ± 1.7	45.0 ± 1.9
Pyruvic kinase	64.7 ± 2.1	66.7 ± 1.8	96.7 ± 1.6	99.9 ± 1.6
γ-glutamyl transpeptidase	1.66 ± 0.12	1.72 ± 0.07	0.90 ± 0.06	0.85 ± 0.17
Aminopeptidase	3.50 ± 0.15	3.54 ± 0.13	1.67 + 0.08	1.62 ± 0.09
Alkaline phosphatase	10.4 ± 0.79	12.8 ± 0.63	11.3 ± 0.6	10.7 ± 0.15

Mean ± SEM for 3 experiments of 6 fish

TABLE 6

The activity of enzymes of glycolysis and of membranes in fish tissues following exposure to mercury (30 µg/1) for 6 weeks

	Enzyme Activity (µmoles/mg protein/hr)			
	LIVER		MUSCLE	
	Control	Mercury	Control	Mercury
Glyceraldehyde-3-phosphate dehydrogenase	10.4 ± 0.6	6.0 ± 0.6	13.8 ± 0.6	10.5 ± 0.01
Lactate dehydrogenase	48.0 ± 0.6	39.6 ± 1.2	41.4 ± 3.0	31.2 ± 0.6
Aldolase	9.07 ± 0.14	8.13 ± 0.15	44.8 ± 1.7	41.4 ± 1.8
Pyruvic kinase	61.6 ± 1.4	62.6 ± 1.3	97.6 ± 1.16	94.9 ± 1.5
γ-glutamyl transpeptidase	1.65 ± 0.07	1.48 ± 0.14	0.93 ± 0.03	0.78 ± 0.04
Aminopeptidase	3.22 ± 0.14	3.32 ± 0.10	1.46 ± 0.05	1.47 ± 0.06
Alkaline phosphatase	9.67 ± 0.40	13.5 ± 0.68	9.09 ± 0.49	9.76 ± 0.38

Mean ± SEM for 3 experiments of 6 fish

TABLE 7

The activity of enzymes of glycolysis and of membranes in perch from impacted lake compared to goldfish

	Enzyme Activity (μmoles/mg protein/hr)			
	LIVER		MUSCLE	
	Control	Impacted	Control	Impacted
Glyceraldehyde-3-phosphate dehydrogenase	10.3 ± 0.2	6.96 ± 0.3	14.5 ± 0.8	11.8 ± 0.3
Lactate dehydrogenase	51.2 ± 3.6	44.8 ± 3.1	42.8 ± 2.1	39.2 ± 2.1
γ-glutamyl transpeptidase	1.81 ± 0.09	1.72 ± 0.06	0.91 ± 0.09	0.96 ± 0.09
Alkaline phosphatase	10.9 ± 0.27	12.1 ± 0.28	13.4 ± 0.42	10.3 ± 0.67

Mean ± SEM for 3 experiments of 6 fish

TABLE 8

The activity of enzymes of glycolysis and of membranes in perch from a clean lake compared to an impacted lake

	Enzyme Activity (μmoles/mg protein/hr)			
	LIVER		MUSCLE	
	Control	Impacted	Control	Impacted
Glyceraldehyde-3-phosphate dehydrogenase	10.5 ± 0.3	7.8 ± 0.4	14.3 ± 0.9	12.1 ± 0.6
Lactate dehydrogenase	40.2 ± 1.8	34.2 ± 2.4	46.8 ± 1.2	46.2 ± 6.6
γ-glutamyl transpeptidase	1.51 ± 0.06	1.65 ± 0.07	1.05 ± 0.08	0.87 ± 0.02
Alkaline phosphatase	9.77 ± 0.43	10.9 ± 0.11	10.8 ± 0.39	10.6 ± 0.77

Mean ± SEM for 3 fish

TABLE 9

Hg levels (ppm) in fish

determined at Ontario Ministry of the Environment Laboratories

Table No.	3	4	5	6	7	8
	3 wk	6 wk	3 wk	6 wk		
Hg Conc.	0.25 μg/l		30 μg/l		Impacted Lake	Impacted Lake
Control Fish	0.01	0.02	0.03	0.02	0.02	0.07
Exposed Fish	0.03	0.04	2.9	8.0	0.16	0.16

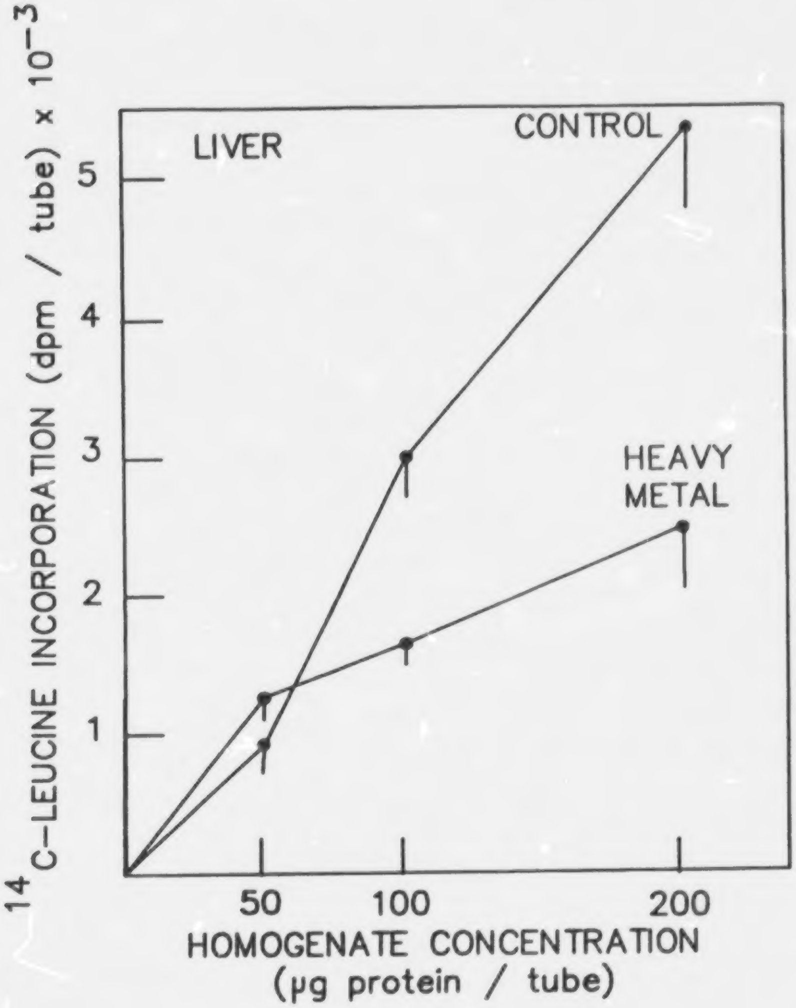


Fig. 1. Activity of soluble fraction of liver in protein synthesis in fish exposed to 0.25 μg/l Hg.

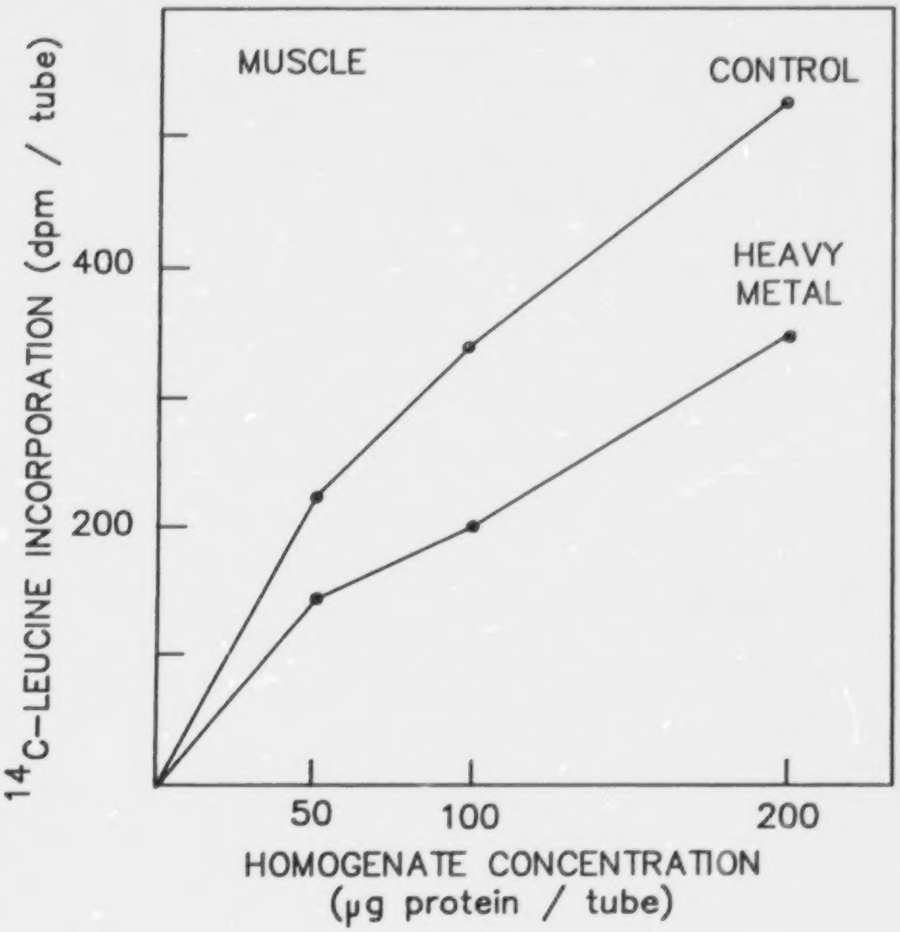


Fig. 2. Activity of soluble fraction of muscle in protein synthesis in fish exposed to 0.25 µg/l Hg.

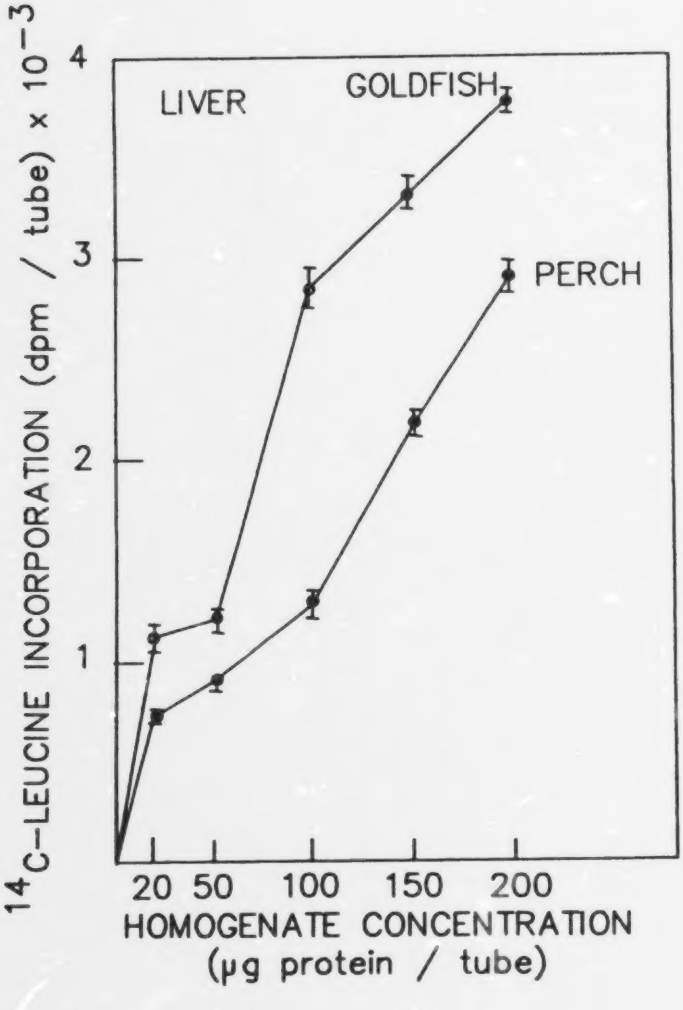


Fig. 3. Activity of soluble fraction of liver in protein synthesis in fish obtained from an impacted lake.

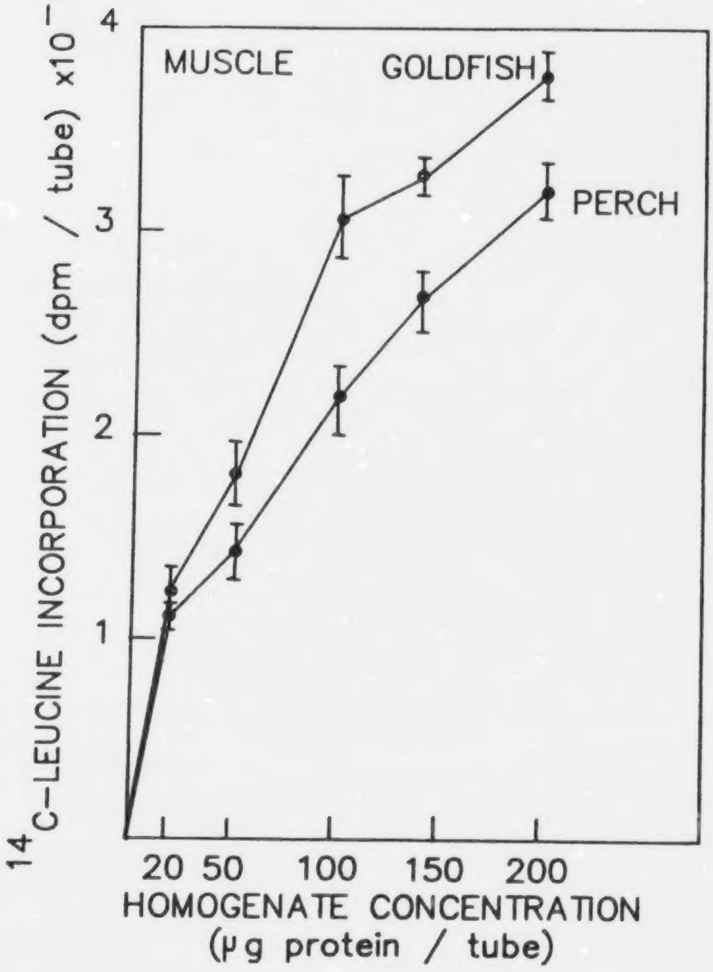


Fig. 4. Activity of soluble fraction of muscle in protein obtained in fish from an impacted lake.

Fig. 5

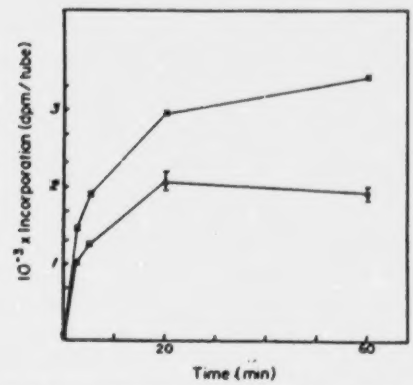


Fig. a. The incorporation of [^{14}C]leucine into protein using polysomes from the liver of turpentine treated rats. Liver polysomes (250 μg RNA/tube) were incubated with control liver postmicrosomal supernatant fraction (450 μg protein/tube) at 37°C for varying times. The reaction mixture contained in a final volume of 0.4 ml the following: 50 mM Tris–HCl buffer (pH 7.7), 80 mM potassium acetate, 5 mM magnesium acetate, 20 mM 2-mercaptoethanol, 5 mM ATP, 0.5 mM GTP, 5 mM creatine phosphate, 50 μg/tube creatine kinase and 0.25 μCi [^{14}C]leucine. The reaction was stopped with the addition of 3 ml 10% (w/v) trichloroacetic acid containing unlabelled carrier leucine and bovine serum albumin. The protein was heated at 90°C, washed and counted for radioactivity as described previously (Sauvé and Nicholls, 1981). Mean ± SE. (○) Control; (●) turpentine

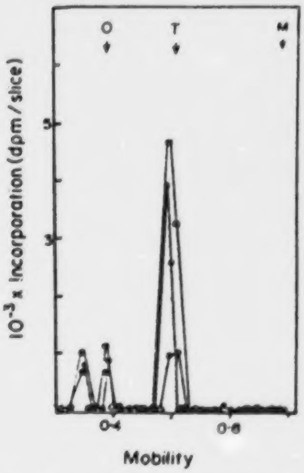


Fig. b SDS gel electrophoresis of liver proteins synthesized from [^{14}C]leucine in an mRNA-dependent reticulocyte lysate. Following incubation of 20 μg RNA in the lysate mixture for 1 hr at 25°C, 20 μl lysate was heated in sample buffer containing SDS and 2-mercaptoethanol and subjected to polyacrylamide gel electrophoresis. Control gels received 2050 dpm, "turpentine" gels received 3900 dpm and "methylmercury" gels received 4320 dpm. Markers were ovalbumin (○), trypsinogen (T) and metallothionein (M). (○) Control; (●) turpentine; (■) methylmercury.

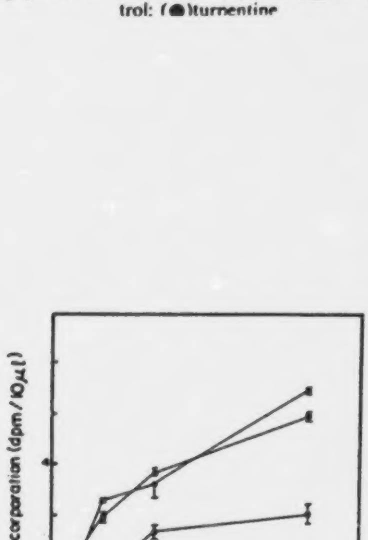


Fig. c. The incorporation of [^{14}C]leucine into protein in an mRNA-dependent reticulocyte lysate using RNA preparations from liver of rats treated with turpentine or methylmercury. Incubation was as described in Materials and Methods in 50 μl final volume. Mean ± SE. (○) Control; (●) turpentine; (■) methylmercury.

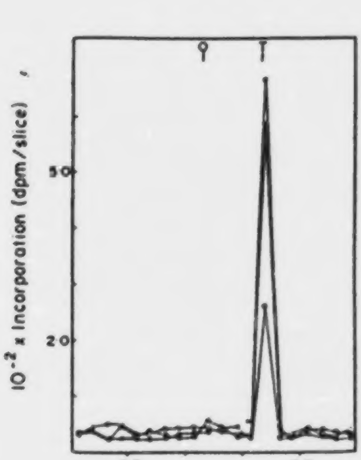


Fig. d Analysis of the mRNA translation product following immunoprecipitation with antiserum to α_1-acid glycoprotein. The immunoprecipitates, prepared as described in Materials and Methods, were either counted or were placed in sample buffer for SDS polyacrylamide gel electrophoresis. Control gels received 2440 dpm, "turpentine" gels received 3800 dpm and "methylmercury" gels received 4800 dpm. Markers and symbols as in Fig. c.

Fig. 5

RESULTS

Liver and muscle enzymes:

These results are shown in Tables 1-8 and can be summarized as follows:-

Pb exposure of 100 or 500 μg/l for 3 to 6 weeks resulted in statistically significant changes in the activities of liver lactate dehydrogenase and muscle glyceraldehyde-3-phosphate dehydrogenase, and liver membrane enzymes exhibited increased activities. Pb exposure of 5 μg/l for 20 weeks exerted no effect on the enzyme activities. However, Pb exposures of 25 μg/l for 6 weeks in combination with 0.25 μg/l Hg and 0.25 μg/l Cd resulted in significant decreases in the activities of muscle glycolytic enzymes and increases in liver membrane enzymes.

Similar changes in liver and muscle glycolytic and membrane enzymes were found in fish exposed for 3 or 6 weeks to 30 μg/l Hg alone. An exception was that with Hg exposure, the activity of γ-glutamyl transpeptidase was decreased significantly in muscle though alkaline phosphatase activity was increased in the liver. Fish from the impacted lake exhibited a statistically significant decrease in the activity of glyceraldehyde-3-phosphate dehydrogenase and lactate dehydrogenase in liver tissue, while the membrane enzymes were very little affected.

Liver and muscle-protein synthesis:

These results are illustrated in Figs. 1-5 and can be summarized as follows:-

Fish exposed to Hg (0.25 µg/l) for six weeks exhibited statistically significant decreases in the enzymes of protein synthesis both in the liver, and also in the muscle, thus indicating an important reduction in the capability for gowth. Fish from impacted lakes showed similar results.

In the continuous flow assay, low levels of Hg (e.g. 5.0 µg/l) trigger mRNA in fish liver for such activities as "acute phase" reactants[17] and metallothioneins.[18] These changes were analyzed by separating newly labelled proteins by polyacrylamide gel electrophoresis.

In experiments studying protein synthesis in young rats we have recently established that Cd and methylmercury exposure result in the stimulation of α_1-acid glycoprotein, an "acute phase" reactant, believed to play a role in response to injury and/or inflammation.[17,18] Further evidence for such a response in fish is currently being examined (Fig.5).

DISCUSSION

Our results for alkaline phosphatase activity in goldfish muscle and liver following low level Hg exposure, coupled with Cd and Pb, or following 30µg Hg/l, are not in good agreement with recent observations of Sastry and Subhadra (1985)[12] who studied the effects upon freshwater catfish of exposure to high levels of Cd (260 µg/l) for 2-8 weeks. They noted decreased activity of alkaline phosphatase activity in liver as well as kidney and intestine. In contrast, the activity in muscle was increased. Our results for 3 or 6 weeks Hg exposure show trends in the opposite direction.

Thus the changes we have observed in our experiments were marked and the identical trend found in goldfish was found in perch collected from an impacted lake.

By 8 weeks' exposure to this level of Cd, Sastry and Subhadra (1982)[13] previously noted an inhibition in the activities of lactate dehydrogenase (and succinic dehydrogenase) in liver and muscle, in contradiction to changes after 2 or 4 weeks. Thus the results for goldfish after Hg exposure and Pb exposure for 3 or 6 weeks resemble the long term effect of Cd exposure which they reported. Most significantly, the observations of Sastry and Rao (1984)[14] in the freshwater murrel exposed for long periods (17 weeks) to Hg (2.2 μg Hg/l) included decreased activity of lactate dehydrogenase in liver and muscle. Our results for Hg and for Pb are also in accordance with acute sublethal exposures of killifish reported by Jackim et al. (1970)[15].

In comparing Tables 3 and 4 with Figs. 1 and 2, it is clear that some statistically significant decreases in glycolytic enzymes could be detected but that the effect on the soluble machinery of protein synthesis was much more dramatic. Similarly, in comparing Tables 7 and 8 with Figs. 3 and 4, the effect on the soluble machinery of protein synthesis was much more dramatic than that on glycolytic and membrane enzymes. This is not so surprising when we remember that the soluble aminoacyl-tRNA synthetases and the soluble elongation factors are very "fragile" enzymes and readily affected by interference with sulphydryl groups in their structure. Thus, these proteins are prime targets for heavy metal effects.

The messenger RNA also is readily affected. It is induced by the "stress" of heavy metal exposure. Thus, the induction of metallothioneins and acute phase reactants in mammalian liver, and most likely in a wide range of fish, by heavy metal exposure is another type of genetic effect.[8,11,16-19] Our experiments with methylmercury show that rat liver DNA is stimulated, perhaps owing to a breakdown of membranes and consequent cell damage,[18] to release more translatable messenger RNA coding for α_1-acid glycoprotein.[11] Since this liver translation product is released to the blood, this acute phase reactant could be a useful indicator of heavy metal toxicity. In this regard, there is evidence that this protein is produced by Pb and Cd exposure, as well as methyl Hg exposure.

The paradox that the soluble protein synthesis machinery of the liver shows decreased activity while certain messenger RNA species show increased activity is seen in mammalian liver as well as in fish. It occurs as a result of the stimulation of the expression of specific genes, on the one hand, balanced by heavy metal suppression of the activity of the (sensitive) enzymes of the protein synthetic machinery, on the other hand.

Smith (1981)[20] proposed that the difference between fasted and fed synthesis rates measured *in vivo* in rainbow trout could be used as a measurement of potential growth rate for species. The liver and gill synthetic rates were unaffected by 15 days starvation while muscle protein synthesis fell from 0.38% (of total muscle protein synthesized per day) to 0.09%, an 80% decrease. Since the growth of various fish species is reduced by exposure to Hg, Cd or other heavy metals, in laboratory controlled experiments, it is not surprising that we find decreased activity of muscle protein synthetic machinery as tested *in vitro*. This technique is much simpler than the *in vivo* measurements and, more importantly, groups of fish can be pooled, from collections from clean and impacted lakes, to give indications of growth impairment and of environmental pollution.

ACKNOWLEDGEMENTS

We gratefully acknowledge the assistance of K. Suns, Ontario Ministry of the Environment. The expert technical help of Andrea Miller, Susan Shepherd and Kathleen Lundy was much appreciated.

REFERENCES:

1 NICHOLLS, D.M., KULISZEWSKA, K., KULISZEWSKI, M.J. and GIRGIS, G.R. Canadian Congress of Biology, London, June 1985.

2 PATNODE, R., BARTLE, E., HILL, E.J. LEQUIRE, V. and PARK, J.H. (1976) J. Biol. Chem. 251: 4468-4475.

3 KORNBERG, A. (1955) Methods in Enzymology 1: 441-443.

3a BUCHER, T. and PFLEIDERER, G. (1955) Methods in Enzymology 1: 435-440.

4 GLOSSMAN, H., and NEVILLE, D.M. Jr. (1972) FEBS Lett. 19: 340-344.

5 PFLEIDERER, G. (1970) Methods in Enzymology 19: 514-521.

6 QUIRK, S.J. and ROBINSON, G.B. (1972) Biochem. J. 128: 1319-1328.

7 LOWRY, O.H., ROSEBROUGH, N.J., FARR, A.L. and RANDALL, R.J. (1951) J. Biol. Chem. 193: 265-275.

8 SAMJI, S., KULISZEWSKI, M.J., GIRGIS, G.R. and NICHOLLS, D.M. (1985) Can. J. Biochem. Cell Biol. 63: 913-918.

9 SAUVÉ, G.J. and NICHOLLS, D.M. (1981) Int. J. Biochem. 13: 981-990.

10 HARRISON, R.E. and NICHOLLS, D.M. (1985) Proc. Can. Fed. Biol. Soc. 28: 220.

11 HARRISON, R.E. and NICHOLLS, D.M. (1986) Comp. Biochem. Physiol. C. In Press.

12 SASTRY, K.V. and SUBHADRA, Km. (1985) Environ. Res. 36: 32-45.

13 SASTRY, K.V. and SUBHADRA, Km. (1982) Toxicol. Lett. 14: 45-55.

14 SASTRY, K.V. and RAO, D.R. (1984) Environ. Res. 34: 343-350.

15 JACKIM, E., HAMLIN, J. and SONIS, S. (1970). J. Fish. Res. Board Canada 27: 383-390.

16 ZAK, I. and DUBIN, A. (1978) Toxic. Appl. Pharmac. 46: 803-805.

17 KOJ, A. (1983) In: Pathophysiology of Plasma Protein Metabolism (ed. Mariani, G.) pp. 221-248, MacMillan, London.

18 DESNOYERS, P.A. and CHANG, L.W. (1975) Envir. Res. 9: 224-239.

19 ROCH, M. and McCARTER, J.A. (1986) Bull. Environ. Contam. Toxicol. 36: 168-175.

20 SMITH, M.A.K. (1981) J. Fish Biol. 19: 213-220.

21 FAUCONNEAU, B. and ARNAL, M. (1985) Comp. Biochem. Physiol. 82A: 179-187.

In situ assessment of mixed copper and zinc impacts on white sucker (*Catostomus commersoni*) populations in several Northern Ontario lakes.

K.R. Munkittrick and D.G. Dixon
Biology Dept., University of Waterloo, Waterloo, Ontario N2L 3G1

This project was undertaken as an integrated field-laboratory program designed to determine the impacts of copper and zinc contamination on white sucker (*Catostomus commersoni*) populations of several lakes in the Manitouwadge district of Ontario. Lakes were evaluated on the basis of accessibility, preliminary sample collections and historical metal status. Manitouwadge Lake (MAN) was selected as the lake with elevated levels of metals, Little Manitouwadge Lake (LMN) was selected as the moderately contaminated site and Loken Lake (LOK) was selected as the control site (Figure 1). The lakes are very similar but differ in metal levels, most notably copper and zinc. Mean assayed copper concentrations (ug/l,std.dev.,n.) were 15.3 for MAN (4.2,35), 13.3 for LMN (3.7,21) and less than 2.0 ug/l for LOK. Mean zinc concentrations (ug/l,std.dev.,n) were 253 for MAN (62.4,35), 209 for LMN (20.3,21) and 26.1 for LOK (22.4,11).

Fish were collected by gillnet (3.5", 8.9 cm monofilament mesh) during the postspawning (POST) and recrudescence (RECR) periods during 1985 and 1986, and during the prespawning (PRES) and spawning (SPAW) periods of 1986. The gillnets were lifted every 40-60 min and the fish were sampled as soon as possible. The fish were weighed to the nearest 5 g and the standard length was recorded to the nearest 0.5 cm. Ages were estimated by pectoral ray sections, and fish older than 9 years were pooled.

Age, weight and length data for the metal contaminated sites were combined since there was no difference in the relationship of age with either weight ($p=.156$) or length ($p=.479$). At age 4 there were no significant differences in either length or weight between the control and metal sites (Figure 2), but control females were longer and heavier than metal fish at all ages older than 5. Results were similar for males (Figure 3).

Most of the individuals in these populations mature between 4 and 6 years of age, and contaminated fish are similar to control fish in length and weight until this age range. At LOK, 40.6 % (13/32) of the 4 and 5 year old female fish captured during PRES were immature and two 5 year old females captured during POST had failed to release their eggs. At MAN one 6 year old female, and two males of ages 5 and 7 were immature, while 6/19 (31.6%) females between the ages of 4 and 7 captured during POST had failed to release their eggs (two 4 year olds, one 5 and three 7). It appears that after attaining maturity, the metal contaminated fish are unable to meet the energetic requirements of both reproduction and growth. The increased impact on females supports this hypothesis since females require more energy for reproduction than males.

No effects of sex or season were found for condition factor ($k=100{*}wt/l^3$) ($p=.66,.29$), but condition factors of MAN fish (2.06,.02,108) were significantly less than LOK (2.15,.02,112; $p<.05$), although neither site was significantly different from LMN (2.11,.02,129; $p>.05$). The increased k of LOK fish suggests that these fish put on proportionally more weight for increments in length.

Overall, the age of MAN fish (6.58,.18,106) was not significantly different from LOK (6.34,.20,110), although LMN fish were slightly older (7.13,.15,125) ($p=.009$). The migrations of older fish at spawning times confounded the results of sex and site, and both MAN and LOK sites showed no effects of sex on age ($p=.54,.42$) and increases in the presence of males during the prespawning period (Table 1).

There were significant effects of sex, site and season on the hepatosomatic index (HSI). Female fish (mean,s.e.,n; 1.51,.04,86) had a larger liver than male fish (1.32,.04,71; p<.0001). LOK fish had a smaller liver (1.28,.05,46) than either MAN (1.43,.05,50) or LMN fish (1.53,.05,61) (p=.0056), and RECR fish had a smaller liver size (1.09,.05,50) than either PRES (1.53,.03,67) or POST fish (1.65,.05,40) (p<.0001). Effects of metal contamination on liver size have been previously reported, although the significance awaits the completion of further analysis.

There was no effect of site on either male (p=.299) or female gonadosomatic index (GSI; p=.355) (GSI=100*gonad wt/body wt) during maturation. As would be expected, there was a highly significant effect of season on both the male and female GSI (p<.0001). The large proportion of MAN females which failed to release their eggs can not be ignored and has been reported before for fish collected from metal contaminated lakes (McFarlane and Franzin, 1980). However, 2/30 control females also failed to spawn, and egg retention has been found in populations of white suckers from Lake Ontario (C. Portt, pers. comm.). The age of the fish which failed to spawn (mean=5.5) suggests that these fish may have been attempting to spawn for the first time. Although the significance of this finding is not clear at this time, we can not attribute the result solely to the impact of metal contamination.

Control fish had significantly higher fecundity (31200, 2619,19) than either MAN (22635,746,26) or LMN fish (21863,958,22) (p<.0001) at similar ages (LOK 7.0,2.0,20, MAN 6.9,1.8,26, LMN 7.3,1.0,24). Although, the fecundity of all fish showed highly significant positive relationships with length and weight, only LOK fish showed a positive relationship with age. Fecundity at both metal contaminated sites showed no relationship with age (Table 2) and is a reflection of the failure of these fish to show increases in weight or length after attaining sexual maturity. The inability of these fish to increase their fecundity with age could have serious consequences on the structure of the populations. Analysis of Lake Ontario samples is presently underway.

At spawning time, eggs were collected from individual females at each collection site, fertilized in duplicate with a pool of milt, water hardened and incubated in clean water before transportation to the University of Waterloo. For the first trials, control eggs were collected from a spawning site on Straight Lake (STR), a small lake adjacent to the Loken site. There was no significant difference in fertilization rate between MAN (79.7,5.5,20) and STR (82.2,1.7,20) (p=.590). Individual males were used to fertilize pools of eggs at each site and MAN estimates (87.7,2.3,20) were lower than STR (92.8,0.8,20) (p=.019), but identical trials using milt from LMN found the opposite to be true. Cross fertilization of LOK eggs with LMN milt yielded fertilization rates of 83.7% (3.3,24) while the fertilization of the identical batch of eggs with LOK milt yielded lower rates (67.2,1.8,20; p<.0001). At the MAN site, enormous numbers of eggs were present on the stream beds, whereas few accumulations of eggs were present at the control site. It was not possible to collect large numbers of eggs from the control site redds so a pooled sample was necessary (156 eggs from 10 redds). There was no impairment of the fertilization process in gametes collected from the metal contaminated sites. The fertilization rates of eggs collected from 10 redds at MAN were 78.3% (7.6) while the fertilization rate of the pooled LOK sample was 78.0%.

The milt volumes of male suckers were significntly higher at both the MAN and LMN site than at either LOK or Lake Ontario collections (p=.009), but there was no difference in the concentration of sperm cells (spermatocrit; p=.672). There was no effect of milt volume or sperm concentration on the fertilization rate using either LMN milt (p=.17,.07) or LOK milt (p=.90,.35).

MAN larvae were significantly shorter (10.48 mm, 0.10,30; p=.008) and lighter (6.6 mg, 0.2,30; p=.011) than the LOK larvae (10.85 mm, 0.12,30; 7.3 mg,0.3,30) at 2 d post-hatch.

The rate of deformation was 3.78% for MAN and 2.50% for LOK. Eggs collected from the redds and hatched in the lab yielded a deformation rate of 6.0%. A "c" shaped deformity was predominant at the time of hatching, representing 100% of the LOK deformities, 82% of the MAN lab and 87% of the MAN redd deformities. Only 29% of deformities found in Lake Ontario suckers at the time of hatching were of this type. The significance of the higher deformation rate in situ demands further evaluation next year.

Although MAN larvae reached crucial developmental stages at times comparable to LOK larvae, the occurrence of swim bladder inflation, first feeding and yolk sac emptying occurred slightly earlier (Table 3). In addition to the slight increase in developmental rate, unfed MAN larvae died at a faster rate than LOK larvae (Figure 4). All MAN unfed larvae were dead by 29 d ph (post-hatch), while some LOK larvae continued to live until 42 d. Furthermore, an increase in the survival rate of MAN fed larvae over unfed could be detected by 25 d ph, while a similar point for LOK was 34 d ph.

Beginning at 1 d post-hatch (ph), larvae were exposed to waterborne copper in 144 hr continuous flow bioassays. New tests were started every 4 d until 37 d ph. Preliminary bioassays (1985-1986 report) found the 96 h LC50 to be around 350 ppb copper, and the survival times at 900 ppb to be less than 48 hrs. Lethal toxicity did not occur at these concentrations until 9 d ph, and it was necessary to add two additional concentrations (1200,2200 ppb) at this time. Although it was not possible to calculate an accurate LC50 for MAN larvae at this age, LOK larvae showed higher mortality at 2200, 1200 and 900 ppb (Figure 5) (nominal:144hr LC50 1275 (1158-1402); 96 hr 886 (802-978)). Furthermore, the resistance times of MAN larvae to 2200 ppb copper was twice as long as LOK larvae (Figure 6). This suggests that the tolerance and resistance of MAN fish to copper was increased by a factor of at least 2 at this age.

The first mortalities for either larvae did not occur at the lower concentrations until after 9 d ph, the age at which blood is first thought to enter the gill arches (McElman and Balon, 1980). The differences in tolerance and resistance become less apparent as the fish aged and was not detectable at ages of 21 d ph. The food reserves of the larvae are decreasing over this time period, and the yolk sac appears empty at ages of 18-20 d ph. This time period corresponds to approximately halfway through the test started at 17 d ph, and before the test at 21 d ph. These tests show marked differences in both tolerance and resistance of the MAN larvae when compared with earlier tests (Figure 6).

Assays started at 29 d ph showed the resistance of fed fish to be higher than unfed at both sites (Table 4). This was the last day any MAN unfed larvae remained alive. Furthermore, all assays of MAN larvae started after the completion of yolk absorption (18-20 d) showed decreased resistance when compared with larvae tested before this time period (Table 5). If the increased tolerance and resistance of the MAN fish was the result of genetic adaptation, we would expect the increased survival to be evident at all ages tested. Bioassays conducted at 33 d, 37 d and 4 months of age do not show this to be the case. Furthermore, the LT50 at 2200 ppb copper for cross-fertilized larvae at 9 d ph (18.5hrs, 17.2-19.5) was not significantly different from 9 d ph LOK unfed larvae (19.4 hrs, 17.6-21.4), and neither was the mortality rate at 900 ppb (3/10 at 9 d ph). In both cases these resistance times are significantly lower from the larvae from contaminated eggs and milt (9 d fed 44.8 hrs, 42.0-48.0, 9 d unfed 38.4, 36.0-41.0). In fact, the only time periods tested which suggest increases in tolerance and resistance are those conducted during the period of endogenous (yolk) nutrition, suggesting the presence of factors in the yolk which infer an advantage to survival. These factors appear to be maternal in origin and future trials will attempt to identify them.

This study is ongoing, and future research will concentrate on several areas. Body energy stores, tissue metal levels, metal-binding proteins and histological examinations of several species of fish are currently underway. Future collections will involve the examination of several phenomena in more detail.

1) Weight-age relationships: the decreased length, weight, condition factors, fecundity, egg weight, larval size, larval survival and increased larval developmental rate of MAN fish are all consistent with the presence of decreased or impaired energy stores. Recent analysis confirms lower glycogen stores in the livers of metal contaminated fish during the autumn period of gonadal growth. Additional samples are needed to examine the energy and nutrtional balance of the fish.

2) Deformity of larval suckers: The increased milt volume, altered egg density, and decreased egg size in MAN streams (when compared with lab studies) are suggestive of osmoregulatory abnormalities. Examination of the blood ion balance of the fish is currently underway, but it would be valuable to examine the consequences of the further decrease in egg size noted during in situ incubation on the size of the larvae after hatch. Additionally, the increased deformity rate in MAN streams (with respect to lab incubations) should be investigated further.

3) Increased larval tolerance: The increased resistance and tolerance of the MAN larvae appears to be related to a maternal factor present in the yolk. There is a need to examine this phenomenon further through a closer examination of the larval tolerance at the critical period of development (9d -20d ph), including more detailed cross-fertilization experiments.

Acknowledgements

This project was funded through the Ontario Ministry of the Environment (Project 193 R). Our appreciation is extended to Dr. C. Neville for her assistance during the course of this research. Additional financial assistance was received from the Natural Sciences and Engineering Research Council.

References

McElman, J.F. and Balon, E.K. 1980. Env. Bio. Fish 5:191-224.

McFarlane, G.A. and Franzin, W.G. 1980. J. Fish. Res. Bd. Can. 35:963-970.

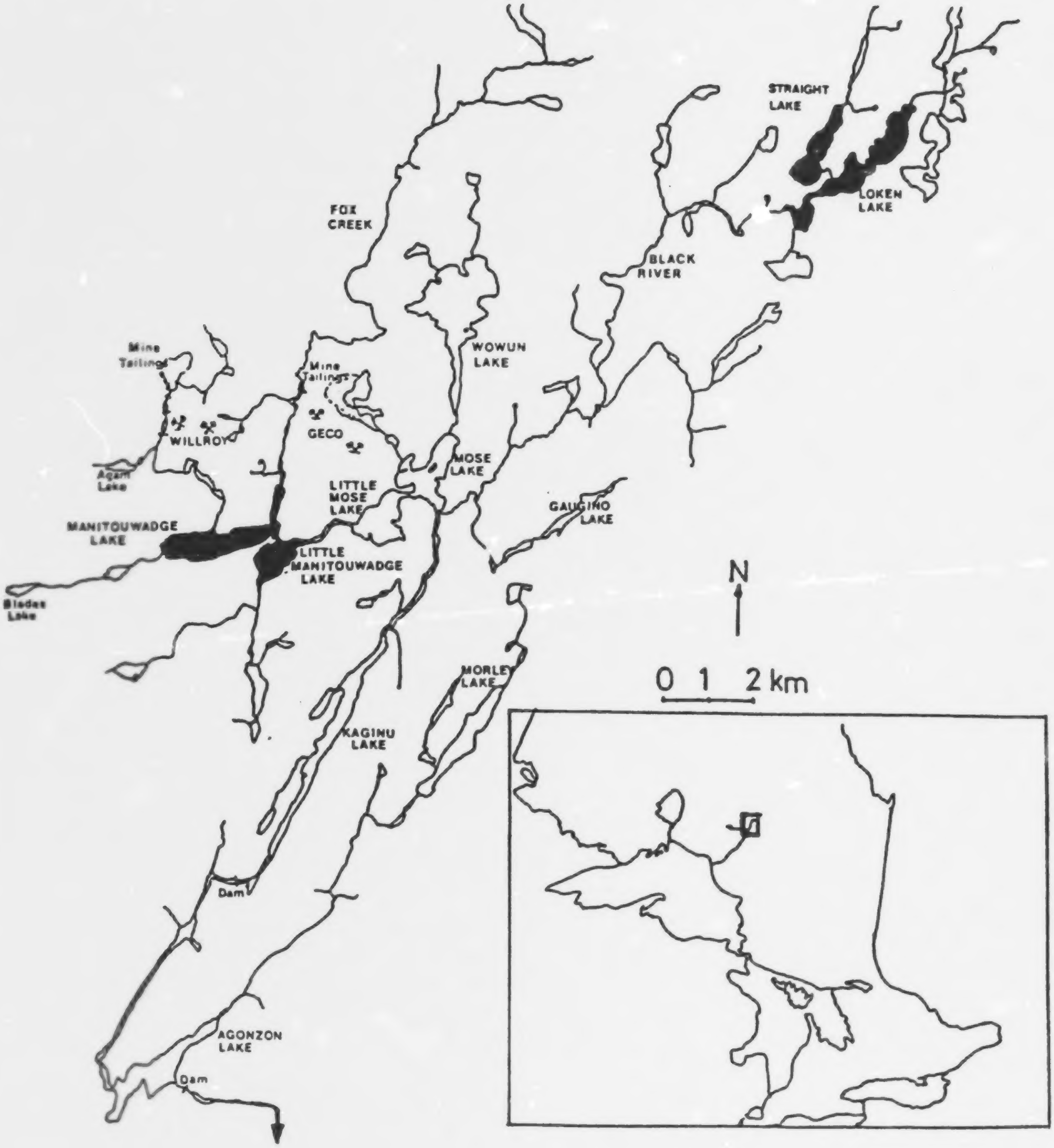


Figure 1. Map of the study site. Manitouwadge Lake represents the elevated metal site, Little Manitouwadge Lake the low metal site and Loken Lake the control site. Water flow is toward the south.

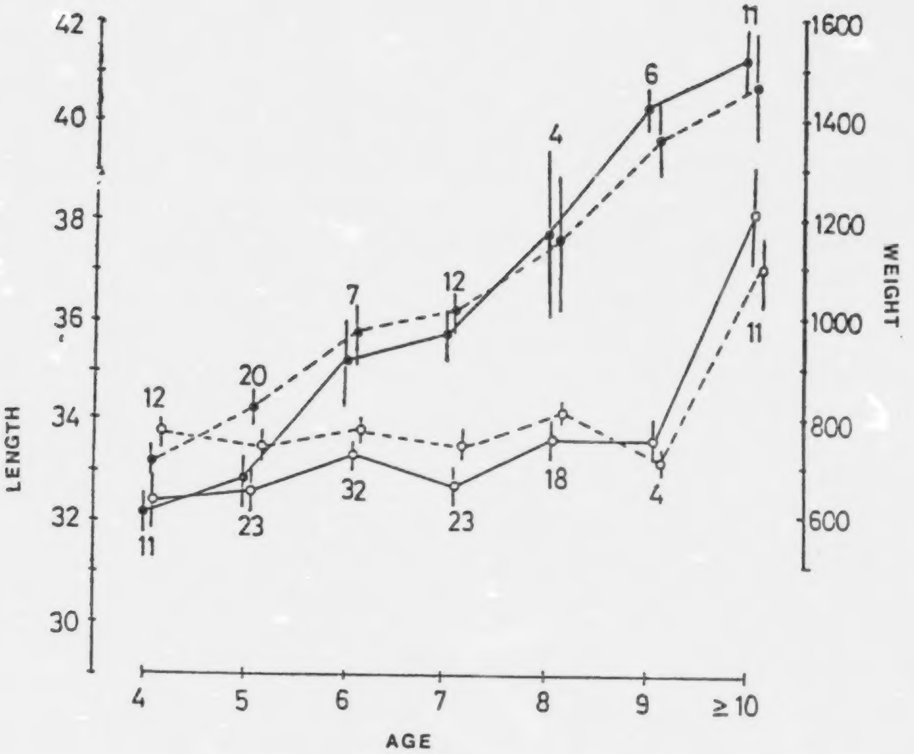


Figure 2. Weight (dotted line) and length (solid line) of female white suckers from the control site (closed circles) and metal sites (open circles). Values represent the mean +/- s.e. with the sample size shown.

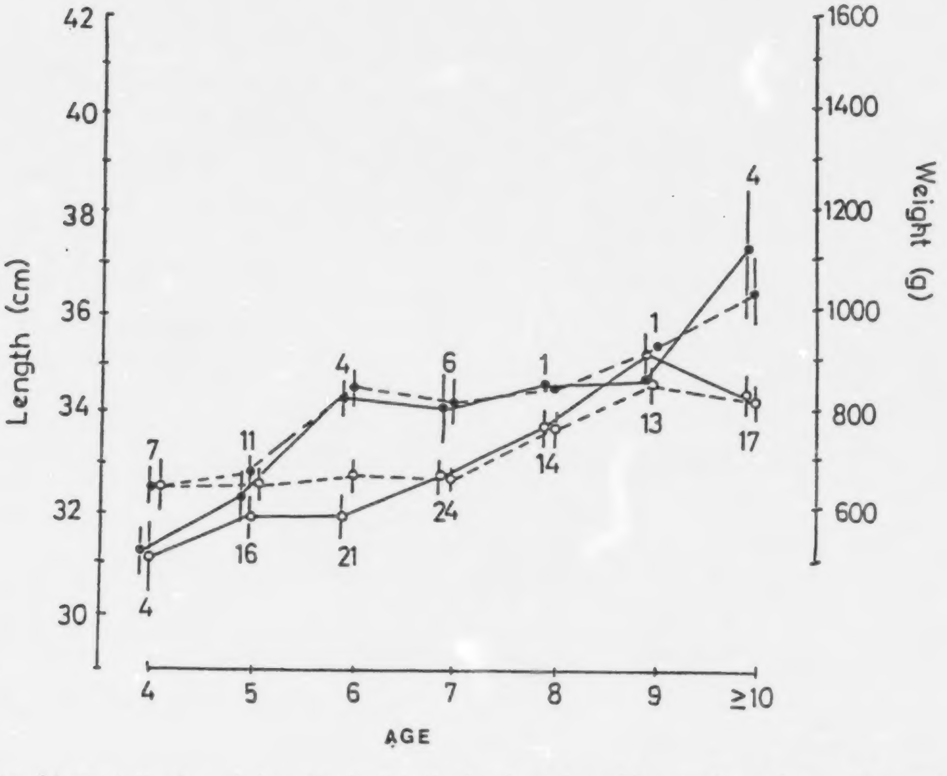


Figure 3. Weight (dotted line) and length (solid line) of male white suckers from the control site (closed circles) and metal sites (open circles). Values represent the mean ÷/- s.e. with the sample size shown.

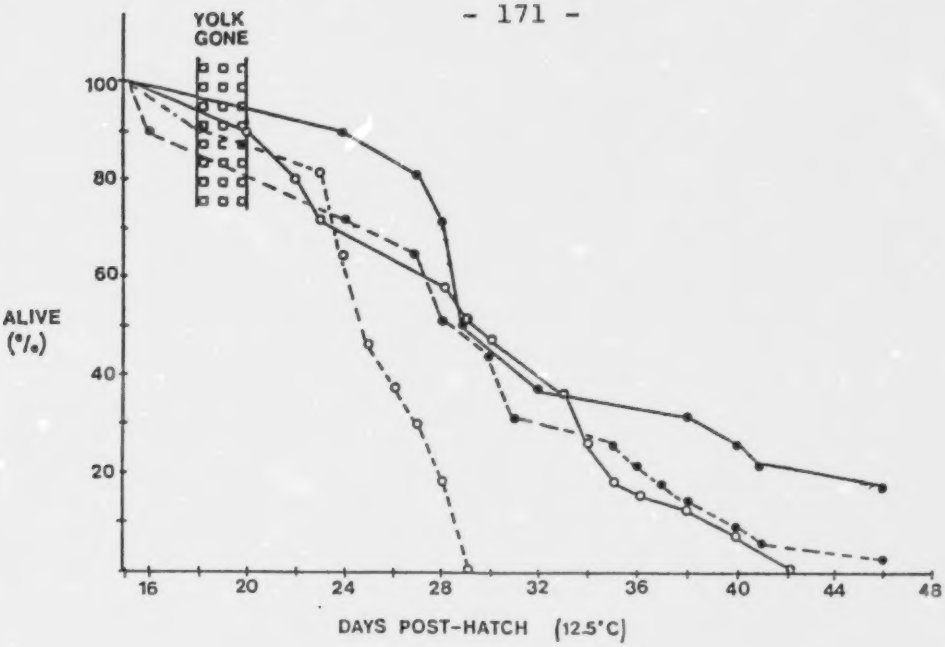


Figure 4. Survival of fed (closed circles) and unfed (open circles) white sucker larvae from the control site (LOK, solid line) and the metal contaminated site (MAN, dotted line). Deaths were calculated from the survival of bioassay control fish and survival was extrapolated from cumulative percent death.

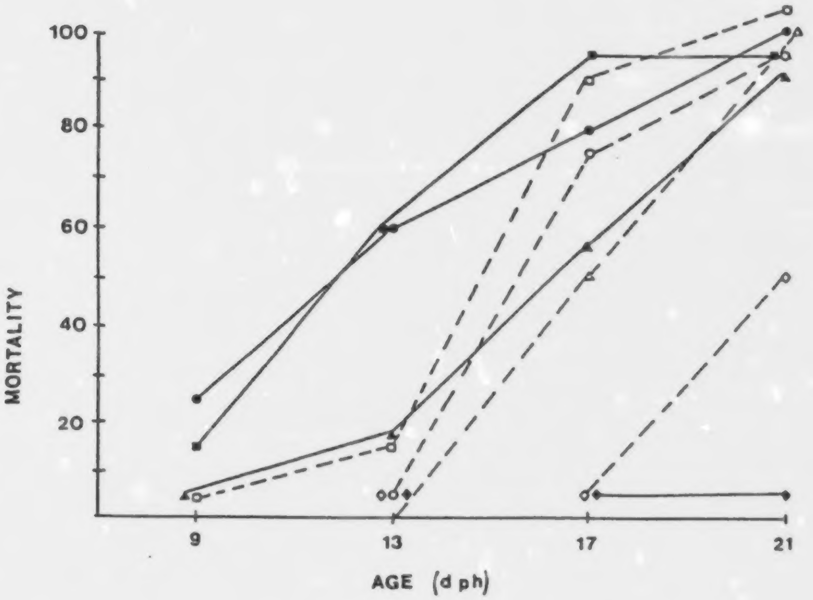


Figure 5. Survival of control (closed symbols) and metal contaminated (open symbols) white sucker larvae after 144 hr exposure to 1200 ppb (circles), 900 ppb (squares) and 600 ppb (triangles) of waterborne copper. Results show combined mortality of fed and unfed larvae (n=20) and diamonds represent control mortality. Age is represented by the age (d) at the start of the bioassay.

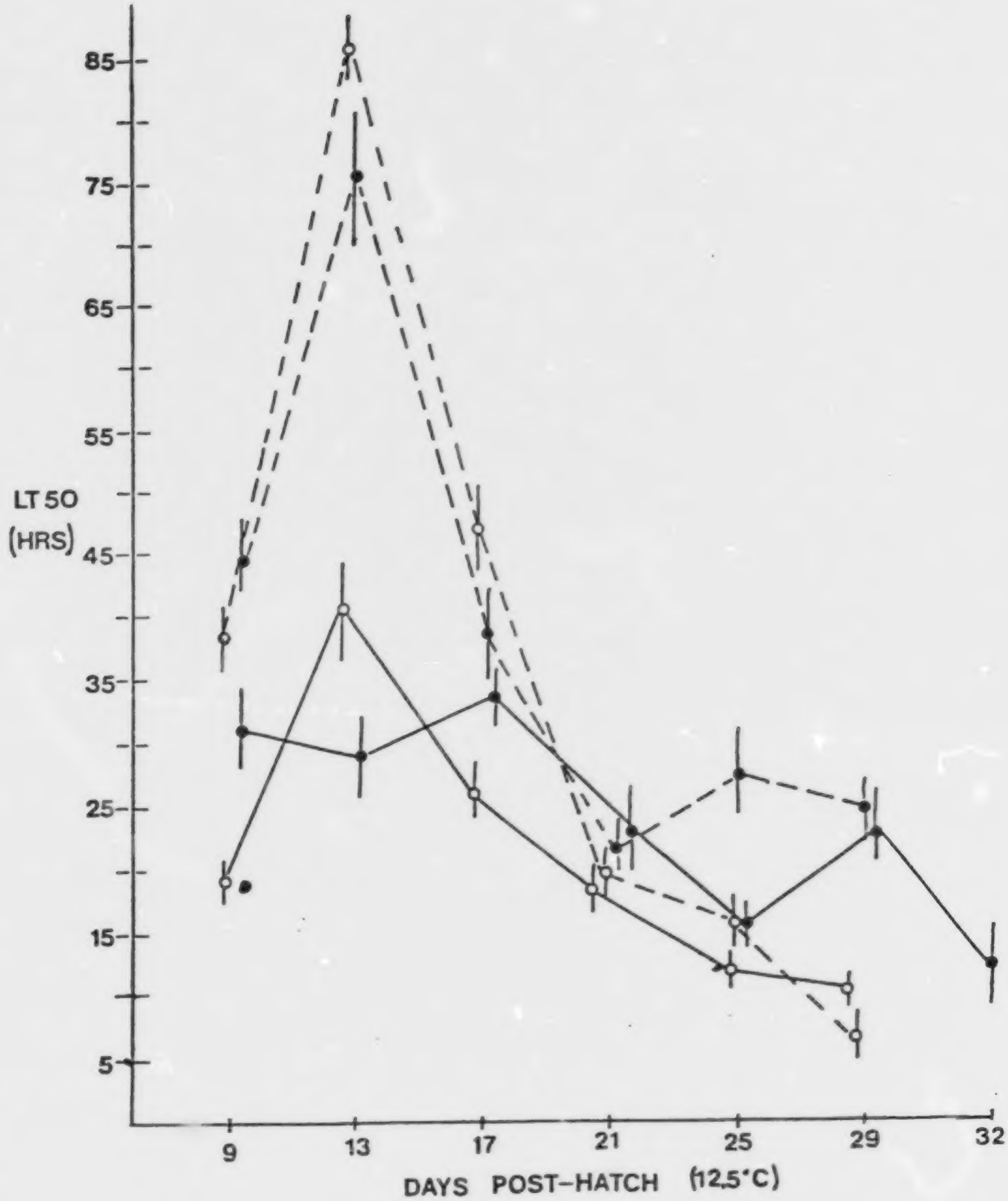


Figure 6. Resistance of white sucker larvae to 2200 ppb of waterborne copper. The time to 50% mortality (hrs) is given for fed (closed circles) and unfed (open circles) larvae from the control site (solid line) and the metal contaminated site (dotted line) at different ages post-hatch. Values are given with their 95% confidence intervals.

Table 1 Ages of white suckers collected from the control site (LOK) and metal contaminated sites. Values are expressed as mean ± s.e. (n), those sharing a superscript are not significantly different (Tukey-Kramer test, $p > .05$) from other values for that site.

		Prespawning	Postspawning	Recrudescence
MAN	male	$7.8 \pm 0.3\ (23)^a$	$6.1 \pm 0.5\ (13)^b$	$6.3 \pm 0.8\ (8)^b$
	female	$7.4 \pm 0.4\ (19)^a$	$6.0 \pm 0.4\ (22)^b$	$5.3 \pm 0.4\ (21)^b$
LMN	male	$7.5 \pm 0.3\ (20)^b$	$7.7 \pm 0.3\ (28)^a$	$7.1 \pm 0.3\ (17)^b$
	female	$7.2 \pm 0.2\ (26)^b$	$6.9 \pm 0.4\ (22)^a$	$5.5 \pm 0.4\ (12)^b$
LOK	male	$6.0 \pm 0.4\ (19)^a$	$7.7 \pm 0.7\ (9)^a$	$4.5 \pm 0.4\ (8)^c$
	female	$6.2 \pm 0.4\ (25)^b$	$7.0 \pm 0.3\ (29)^b$	$6.0 \pm 0.5\ (20)^b$

Table 2. Coefficients for relationships of fecundity (total # eggs) with age, length and weight of control fish (LOK) and fish from metal contaminated sites.

	n	Slope	Intercept	R	R^2	p(Bo = 0)	p(linear)
Age (yr)							
LOK	19	4602.4	-47.7	0.81	.660	.0001	<.001
LMN	22	1183.8	13310	0.27	.072	.226	
MAN	25	741.8	17613	0.34	.118	.093	
Length (cm)							
LOK	19	2259.0	-49708	0.94	0.880	.0001	<.001
LMN	22	1526.9	-29565	0.70	0.489	.0003	<.001
MAN	25	1092.4	-13602	0.63	0.399	.0005	<.001
Weight (g)							
LOK	19	25.92	3454	0.97	0.951	.0001	<.001
LMN	22	20.38	4679	0.80	0.641	.0001	<.001
MAN	25	22.68	5219	0.71	0.510	.0001	<.001

Table 3. Age at which white sucker larvae reach crucial developmental stages from the control (LOK) and MAN. Times are given in days post-hatch and daily temperature units (OTU). The developmental temperature was 12°C, and values are compared with published developmental times (McElman & Balon, 1980: assumes hatch at 5.5 d post-fertilization, developmental temperature was 15°C).

Critical Stage (McElman & Balon, 1980)	DTU	Predicted (12°C)	MAN			LOK		
			Days	DTU	% exhibiting	days	DTU	% exhibiting
I. first swimming (< 2.5cm)	60	5	5	60		5	60	
II. bile in gall bladder gill circullation complete	90	7.5	7	84		7	84	
III. Mouth opening and closing pectorial fins moving, blood into gill arches	120	10	9	108		9	108	
IV. Swim bladder inflated	150	12.5	9	108	30	10	120	5
			11	132	90	12	144	50
			12	144	100	13	156	100
V. peristalsis, first food, first feces	165	13.8	18	216	20	20	240	20
			21	252	100	22	264	100
VI. Yolk gone	225	18.8	18-20	196-204		20	204	

Table 4. Time to 50% mortality (LT50) of white suckers larval exposed to 2200 ppb copper. Values are reported as LT50 (hours) with 95% confidence interval. Values sharing a bar are not significantly different. Data are reported for larval of different ages (days post-hatch). MAN values shown with a star are significantly higher from the control values.

MAN

29d	unfed	6.7	(4.7-9.4)
25d	unfed	*15.9	(14.2-17.8)
21d	unfed	19.1	(16.8-21.7)
21d	fed	21.7	(20.1-23.5)
29d	fed	24.9	(21.9-27.1)
25d	fed	*27.5	(24.3-31.1)
9d	unfed	*38.4	(36-41)
17d	fed	38.4	(34.7-42.5)
9d	fed	*44.8	(42.0-48.0)
17d	unfed	*46.7	(43.3-50.3)
13d	fed	*75.0	(69.0-81.6)
13d	unfed	*85.3	(82.4-88.2)

LOK

29d	unfed	~11	(estimated)
25d	unfed	12.2	(10.8-13.7)
33d	fed	12.3	(9.4-16.1)
25d	fed	15.3	(13.9-16.8)
21d	unfed	18.4	(16.6-20.3)
9d	unfed	19.4	(17.6-21.4)
21d	fed	23.3	(20.1-27.1)
29d	fed	23.4	(20.8-26.1)
17d	unfed	26.3	(24.4-28.3)
13d	fed	29.2	(25.8-33.0)
9d	fed	31.0	(28.6-33.7)
17d	fed	33.9	(31.6-36.3)
13d	unfed	47.0	(36.7-45.0)

Table 5. Further summary of date from Table 4.

MAN

UNFED	FED
29d	21d
25d	29d
21d	25d
9d	17d
17d	9d
13d	13d

LOK

UNFED	FED
29d	33d
25d	25d
21d	21d
9d	29d
17d	13d
13d	9d
	17d

COMBINED

UNFED	FED
MAN 29d	LOK 33d
LOK 29d	LOK 25d
LOK 25d	MAN 21d
MAN 25d	LOK 21d
LOK 21d	LOK 29d
MAN 21d	MAN 29d
LOK 9d	MAN 25d
LOK 17d	LOK 13d
MAN 9d	LOK 9d
MAN 17d	LOK 17d
LOK 13d	MAN 17d
MAN 13d	MAN 9d
	MAN 13d

THE FATE OF TOXIC ORGANIC CHEMICALS IN SEWAGE TREATMENT PLANTS

Brian Clark, Glynn Henry, Donald Mackay, Sandra Salenieks
Institute for Environmental Studies, University of Toronto

ABSTRACT

A predictive model based on the fugacity modelling system, which describes the steady-state fate of organic chemicals in a water pollution control plant has been developed. By estimating a prevailing fugacity in each of the primary, aeration, and secondary settling tanks, chemical concentrations in the water streams, air streams, and sludge streams can be calculated, fluxes can be estimated and a mass balance assembled.

Comparison of the fugacity model with the predictive fate models or sub-models developed by other workers shows good agreement. The fugacity model was also subjected to tests of validity by: (i) conducting laboratory-scale experiments for chemical stripping, stripping-sorption, and stripping-sorption-biodegradation processes; and (ii) comparing the model predictions with data obtained from the literature, from pilot plant studies, and from full-scale water pollution control plants.

The model predicted the fate of organic chemicals with fair accuracy based on reasonable estimates of biodegradation rate constants. It is suggested that when adequately calibrated, the model can be used to give a relatively simple description of the fate of organic chemicals in treatment systems.

INTRODUCTION

Some sixty thousand organic chemicals have been produced commercially and approximately 1200 new chemicals are introduced each year. Many of these chemicals are present in industrial or municipal wastewaters, which are usually treated in a biological oxidation system. The efficiency of these systems is usually expressed as the percent removal of the chemical from the influent stream. This does not necessarily provide information on the amounts of chemical which are biodegraded, stripped or volatilized into the atmosphere, or sorbed onto the biological solids (sludge). A model that predicts the fate of chemicals in a water pollution control plant (WPCP) by determining the amounts and concentrations of the chemical in the effluent, off-gas and waste sludge streams is useful for predicting the true efficiency of the system, as measured by the actual extent of degradation of the chemical in question. It permits assessment of the impact of each waste stream on the environment as a whole by producing a quantitative picture of the chemical's fate.

A predictive fate model has been developed based on the fugacity modelling concept as proposed by Mackay (1). The model was designed to be easy to understand and use. It is programmed in BASIC language, and is compatible with an IBM Personal Computer. The input paramters are the physical properties of the chemical (molecular weight, vapor pressure, solubility in water, octanol-water partition coefficient, and a degradation rate constant), and the relevant operating parameters of the WPCP (process flowrates, volatile suspended solids concentrations, tank surface areas and volumes). The program gives as output a prediction of the chemical fluxes in all process streams, the chemical concentration in the water, air, and sludge phases and a total statement of mass balance.

A second aspect of the study involved the simulation of a biological treatment plant using a laboratory-scale activated sludge plant to determine the applicability or validity of the model, as well as to determine kinetic rate constants, partition coefficients, and mass transfer coefficients for the processes of bio-oxidation, sorption and stripping. The model was also compared to other predictive fate models, and to data from an actual WPCP.

FUGACITY MODEL

The fugacity model describes and predicts the fate of organic chemicals entering a water pollution control plant based on the following assumptions:

1) Equilibrium exists between the water phase and the sludge phase for each tank. In the aeration tank, the off-gas stream is in equilibrium with the water phase.

2) The WPCP is at steady state.

3) The chemical entering the plant is either dissolved in the water or sorbed on to the incoming suspended solids.

4) In both the primary and secondary settling tanks, the sludge blanket volume is ten percent of the total settling tank volume. This estimate is required in order to determine the extent of biodegradation in the settling tanks.

Based on these assumptions, two predictive fate models were developed (to account for either separate waste streams or combined waste streams). By inputting the following parameters, both programs determine the fugacity in each of the process vessels and hence the concentrations and flow rates:

Chemical Properties - molecular weight (g/mol)
- water solubility (g/m^3)
- vapour pressure (Pa)
- log K_{ow} (ie. octanol-water partition coefficent)
- first order biodegradation rate constants in the aeration tank and the primary and secondary settling tanks (h^{-1})

System Properties - volumetricflowrates (m^3/h)and volatile suspended solids concentrations (g/m^3) for:
  - i) influent stream
  - ii) raw sludge stream
  - iii) primary effluent stream
  - iv) mixed liquor stream
  - v) return sludge stream
  - vi) waste sludge stream
  - vii) secondary effluent stream
  - viii) air stream

- tank volumes (m^3)
- primary and secondary settling tank surface areas (m^2)
- MLSS concentration (g/m^3)
- temperature (K)

A full account of the model structure and mathematics is beyond the scope of this report, but reference can be made to Clark (1986) for more detail. A brief review is presented below.

Fugacity and its use in modelling systems has been described in a series of papers by Mackay et al (1). It can be viewed as an escaping tendency of partial pressure. When a chemical such as benzene is in equilibrium between phases such as water, air and biomass, its fugacity is equal in all three phases. Fugacity (f) is related to concentration (C) by the simple expression:

$$C = Zf$$

where Z is a fugacity capacity for the chemical in the particular phase. Procedures have been published by which Z values can be estimated for all relevant phases, mainly from partition coefficients and properties such as water solubility and vapour pressure.

All process rates are expressed as the products of the fugacity in the relevant phase and a D value, ie.,

$$\text{Rate} = Df$$

Procedures for estimating D values have been documented, but a brief review may be useful here.

Reaction or degradation rates can be characterized by a reaction D value defined as VZk, where V is the phase volume, Z is the fugacity capacity and k is the first order rate constant. The group Df is thus equivalent to VCk. This expression is used to describe biodegradation rates. Non-linear kinetics can be included but first-order behaviour is generally assumed to apply to dilute chemical components.

Transfer by flow from vessel to vessel is characterized by a D value defined as GZ, where G is the phase flow rate and Z is the fugacity capacity. The rate Df is thus GC. When the flow is of a mixture (eg. water and biomass), separate D values are defined, then added, and the amounts transported in each phase can be calculated. This expression is used for water, biomass and air flows.

The rate of diffusive transfer between phases such as water and air by evaporation or stripping can be expressed as $D(f_1-f_2)$, where f_1 is the chemical fugacity in the source and f_2 in the destination phase. This is used to describe evaporation, D being defined as:

$$1/D = 1/k_1AZ_1 + 1/k_2AZ_2$$

where k_1 is the water side and k_2 is the air side mass transfer coefficients (units of velocity), A is the interfacial area, and Z_1 and Z_2 are the water and air Z values. This is essentially the Whitman two resistance model as used by previous workers.

For air stripping a similiar approach could be used, but the individual values of k_1, k_2 and A are uncertain and it is useful to define a product of mass transfer coefficient and area. In the interests of simplicity, we assume that the D value is so large that f for air equals that of water, ie. the streams are in equilibrium. Non-equilibrium could be treated by including a suitable D value describing the transfer resistance.

A simple mass balance can be assembled as depicted in Figs. 1 and 2. The various input parameters are used to calculate the D and Z values and the equations solved as shown to give the fugacities. The concentrations can then be calculated as fZ and the flows as Df.

There is no need for the user to understand or use fugacity since this is handled within the program. It is possible to rewrite the equations in Fig. 2 in conventional concentration form, but the final conventional equations are very lengthy. The conventional and fugacity equations are ultimately algebraically identical. The fugacity format equations are more compact and elegant, and with some effort, give more easily understandable results.

Fig. 1: Fate of Organic Chemicals in a Simple Activated Sludge Plant

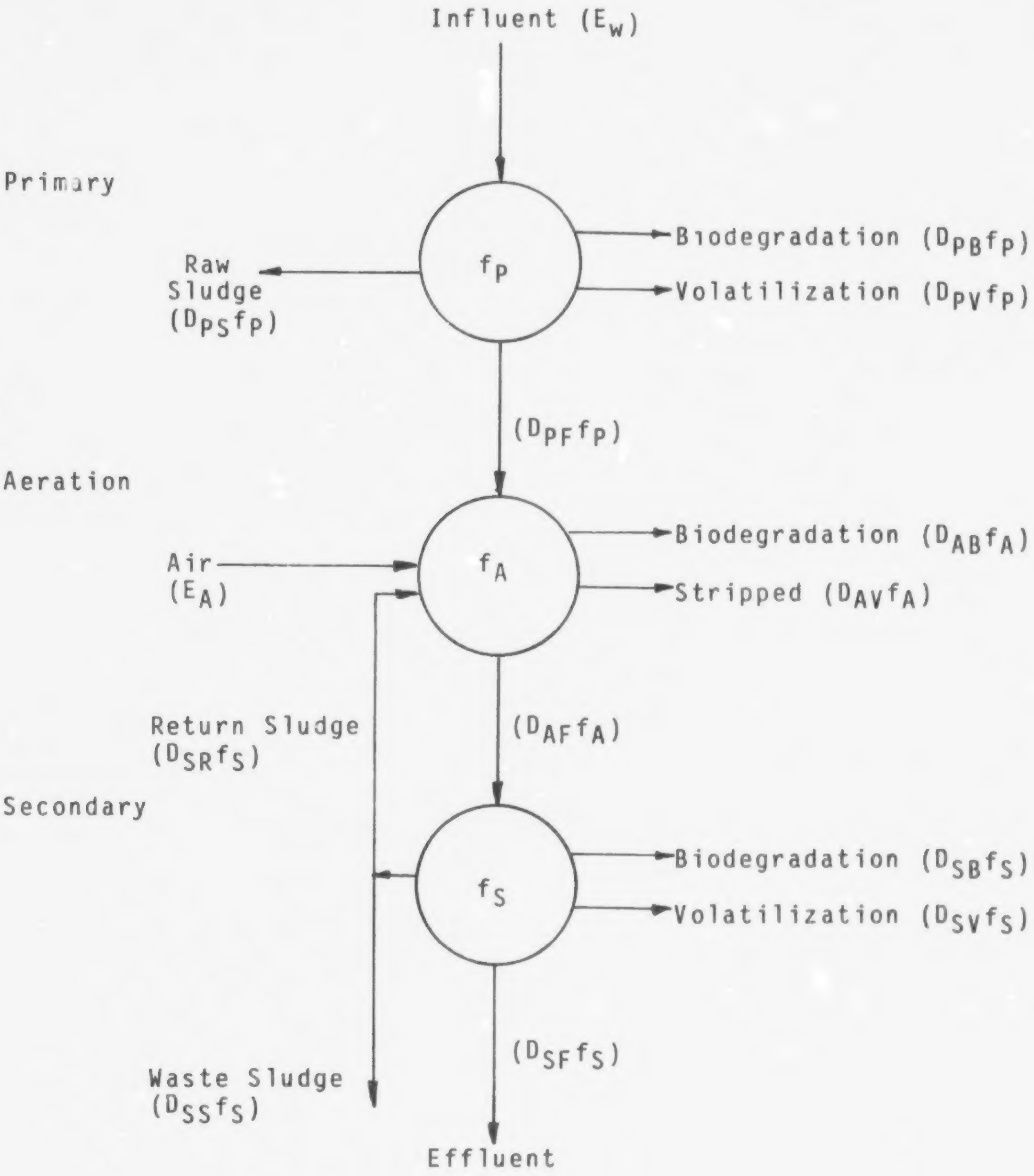

Influent (E_w)
Primary
f_P
Biodegradation ($D_{PB}f_P$)
Volatilization ($D_{PV}f_P$)
Raw Sludge ($D_{PS}f_P$)
($D_{PF}f_P$)
Aeration
f_A
Air (E_A)
Biodegradation ($D_{AB}f_A$)
Stripped ($D_{AV}f_A$)
Return Sludge ($D_{SR}f_S$)
($D_{AF}f_A$)
Secondary
f_S
Biodegradation ($D_{SB}f_S$)
Volatilization ($D_{SV}f_S$)
($D_{SF}f_S$)
Waste Sludge ($D_{SS}f_S$)
Effluent

Fig. 2: Mass Balance Equations

Primary Tank

$$E_W = (D_{PS} + D_{PF} + D_{PB} + D_{PV})f_P = D_{PT}f_P$$

Aeration Tank

$$E_A + D_{PF}f_P + D_{SR}f_S = (D_{AB} + D_{AV} + D_{AF})f_A = D_{AT}f_A$$

Secondary Tank

$$D_{AF}f_A = (D_{SB} + D_{SV} + D_{SF} + D_{SR} + D_{SS})f_S = D_{ST}f_S$$

Solution:

$$f_P = E_W/D_{PT}$$

$$f_A = (E_A + D_{PF}f_A)/(D_{AT} - D_{AF}D_{SR}/D_{ST})$$

$$f_S = D_{AF}f_A/D_{ST}$$

where D_{PT}, D_{AT} and D_{ST} are as defined above.

Sorption to biomass was treated using an approach similiar to Blackburn's (1984), which regards the biomass as consisting of 20% (volume fraction) octanol, and 80% water, ie.,

$$Z_b = 0.2K_{ow}Z_w + 0.8Z_w$$

Biodegradation is treated as a first-order decay process. Rate constants can be defined based on the total chemical concentration or the concentration actually present sorbed onto the biomass.Since most experiments report decay in total concentrations, the former is preferred. The major challenge in modelling WPCPs is to select an appropriate value for this rate constant. The most convenient methods are to select an appropriate half life based on results of bench scale tests, or to fit the model to some actual performance data from pilot or full scale plants. An advantage of the model is that it "subtracts out" the losses attributable to sorption to sludge,

The output from this program can be printed in any combination of the following three forms as shown in Fig. 3:

3A) data sheet
3B) schematic diagram of the WPCP
3C) narrative summary.

Fig. 3A: Data Summary Sheet

```
XYZ

Chemical Properties:


Molecular Weight (g/mol)                                   100
Aqueous Solubility (g/m3)                                  10
Vapour Pressure (Pa)                                       10
                  (atm)                                    9.869232E-05
                  (mm Hg)                                  7.500616E-02
Octanol-Water Partition Coeff (Kow)                        10
LOG Kow                                                    1
Biodegradation Rate Constant (h^-1)
                        -Primary Tank                      .01
                        -Aeration Tank                     .01
                        -Settling Tank                     .01

System Properties:

Primary Tank:

Water Influent Rate (m3/h)                                 1000
Chemical Concentration In Plant Influent (g/m3)            .01
Primary Sludge Removal Rate (m3/h)                         100
Primary Sludge VSS Concentration (g/m3)                    1000
Primary Effluent VSS Concentration (g/m3)                  10
Influent VSS (g/m3)                                        150
Primary Tank Volume (m3)                                   1000
Primary Tank Surface Area (m2)                             100
Hydraulic Retention Time (h)                               1

Aeration Tank:

Air Flowrate (m3/h)                                        1000
Sludge Recycle Rate (m3/h)                                 100
Aeration Tank Volume (m3)                                  1000
MLSS Concentration (g/m3)                                  2000
Hydraulic Retention Time (h)                               1.11
Solids Retention Time (h)                                  18.5
                           (days)                          .771
Temperature ('C)                                           25

Settling Tank:

Waste Sludge Removal Rate (m3/h)                           100
Underflow VSS Concentration (g/m3)                         1000
Effluent VSS Concentration (g/m3)                          10
Settling Tank Volume (m3)                                  1000
Settling Tank Surface Area (m2)                            100
Hydraulic Retention Time (h)                               .99



Tank          Phase     Fugacity           Concentration
                          (Pa)         (g/m3)         (mol/m3)

Primary       Water     9.958018E-03  9.958018E-03  9.958018E-05
              Sludge    9.958018E-03  1.991604E-02  1.991604E-04
Aeration      Air       9.509096E-03  3.83614E-04   3.83614E-06
              Water     9.509096E-03  9.509096E-03  9.509096E-05
              Sludge    9.509096E-03  1.901819E-02  1.901819E-04
Settling      Water     9.488111E-03  9.488109E-03  9.48811E-05
              Sludge    9.488111E-03  1.897622E-02  1.897622E-04

WPCP Mass Balance for XYZ

WPCP Stream Directory:

                                        5
                                        :
                                        :
                 ------          ------        ------
                 :    :    4->   :    :        :    :
             1-> :    :--2-->    :    :--6-->  :    : ->7
                 :    :          :    :        :    :
                 ------          ------        ------
                   :               *              :
                   :               :              :
                   :               ---- 8 -----   :
                   :                              :
                   -> 3                           -> 9

Stream          Stream Flow         Chemical Flow              Percent
 & No.            m3/h        Grams/h          Mole/h

Primary Tank

1. Influent      1000          10               .1               100
2. Effluent      900.1         8.963301         .089633
3. Waste Sludge  100           .9967976         9.967976E-03     9.967976
   Volatilised                 3.989968E-02     3.989968E-04     .3989968
   Biodegraded                 2.987405E-04     2.987405E-06     2.987405E-03

Aeration Tank

4. Air Inlet     1000          0                0
5. Air Outlet    1000          .383614          3.83614E-03      3.836139
6. Mixed Liquor  1000.1        9.529087         9.529087E-02
   Biodegraded                 3.603638E-04     3.603638E-06     3.603638E-03

Settling Tank

7. Effluent      800.1         7.591512         7.591512E-02     75.91512
8. Return Sludge 100           .9497598         9.497598E-03
9. Waste Sludge  100           .9497598         9.497598E-03     9.497598
   Volatilised                 3.801686E-02     3.801686E-04     .3801686
   Biodegraded                 1.897622E-05     1.897622E-07     1.897622E-04
```

Fig. 3B: Schematic Diagram of WPCP

```
                   PRIMARY TANK

                ******************
                * FP (Pa)=        *-> XYZ
                * 9.958018E-03    *   VOLATILIZATION
                *                 *   LOSSES (g/h)
                *                 *   3.989968E-02
                *                 *
                *                 *
                *                 *
     INFLUENT   *                 *
     FLOW ----->*-----------------*-> EFFLUENT
     (g/h)      *                 *   FLOW (m3/h)
     1000       *                 *   900.1
                * CW (g/m3)=      *   XYZ
                * 9.958018E-03    *   MASS FLOW
                *                 *   (g/h)
                *                 *   8.963301
                *                 *
     XYZ        * CS (g/m3)=      *
     (g/h)--->  * 1.991604E-02    *
     10         *                 *
                ******************
                          :
                          :
                          --------> WASTE SLUDGE
                                    FLOW (m3/h)
                                    100
                                    XYZ
                                    MASS FLOW (g/h)
                                    .9967976


                   AERATION                       SETTLING
                    TANK                           TANK

                                AIR FLOW (m3/h)= 1000
                           ---> XYZ
                           :    MASS FLOW (g/h)= .383614
                           :
                           :
               ********************             *****************
               *   FA (Pa)=       *             * FS (Pa)=      *->XYZ
               *   9.509096E-03   *             * 9.488111E-03  * VOLATILIZA
               *                  *             *               * LOSSES (g/
               *                  *             *               * 3.801686E-
               *   CA (g/m3)=     *             *               *
               *   3.83614E-04    *             *               *
               *                  *             *               *
               *                  *             *               *
               *                  * MIXED       *               *
WATER (m3/h)->*-------------------*------------>*---------------*->EFFLUENT
900.1          *                  * LIQUOR      *               * FLOW (m3/h
               *                  * FLOW        *               * 800.1
               *   CW (g/m3)=     * (m3/h)      * CW (g/m3)=    * XYZ
               *   9.509096E-03   * 1000.1      * 9.488109E-03  * MASS FLOW
AIR (m3/h)--->*                   *             *               * (g/h)
1000           *                  *             *               * 7.591513
               *                  *             *               *
XYZ            *   CS (g/m3)=     *             * CS (g/m3)=    *
(g/h)--------->*   1.901819E-02   *             * 1.897622E-02  *
8.963301       *                  *             *               *
               ********************             *****************
                         :                               :
                         :                               :
                         ------- SLUDGE RETURN <--------------> WASTE SLUDG
                                 FLOW (m3/h)                    FLOW (m3/h)
                                 100                            100
                                                                XYZ
                                                                MASS FLOW (
                                                                .9497598

   TOTAL AMOUNT OF DESIGNATED CHEMICAL BIODEGRADED (g/h)= 4.023275E-04
                                        -PRIMARY   (g/h)= 2.987405E-06
                                        -AERATION  (g/h)= 3.803639E-04
                                        -SETTLING  (g/h)= 1.897622E-05
```

Legend:

FP: Fugacity in the primary tank
FA: Fugacity in the aeration tank
FS: Fugacity in the settling tank
CA: Concentration of chemical in air
CW: Concentration of chemical in water
CS: Concentration of chemical in sludge

Fig. 3C: Narrative Summary

Inflow

The chemical of concern enters the plant at a concentration of 0.010 g/m in a total water flow of 1000.0 m3/h. Therefore, 10.000 g/h of the chemical enters the plant.

Primary Settling Tank

During primary treatment, the chemical of concern is 0.02 percent removed due to being sorbed into the volatile suspended solids present in t primary tank. It is estimated that 0.40 percent is volatilized into the atmosphere. Biodegradation accounts for a 0.00 percent reduction of the chemical. This behavior determines the primary effluent concentrati to be 0.0100 g/m3 in the water and 0.01992 g/m3 in the sludge.

Aeration Tank

The primary effluent enters the aeration basin at a flowrate of 900.1 The air flowrate into the tank is 1000.0 m3/h. Under these conditions, the chemical is estimated to be 3.84 percent removed due to stripping and 0.00 percent removed due to biodegradation. This results in a sludge concentration of 0.01902 g/m3 and a water concentration of 0.0095 g/m3. The concentration of the chemical in the off-gas stream is 0.0004 g/m3.

Secondary Settling Tank

After aeration, the mixed liquor, flowing at 1000.1 m3/h into the secondary tank, is allowed to settle. This results in the volatilization of 0.38 percent of the chemical of concern as well as a decrease of 0.00 percent due to biodegradation. It is therefore estimated that the effluent water concentration is 0.0095 g/m3 in a stream flowing at 800.1 m3/h. The underflow is divided into two streams; return sludge and waste sludge which flow at 100.0 m3/h and 100.0 m3/h respectively. The chemical concentration in the sludge is 0.0190 g/m3.

Overall Summary

Assuming that the chemical enters the plant at a flow of 10.0 g/h, 0.78 percent or 0.1 g/h of the chemical will volatilize into the atmosphere, 3.84 percent or 0.4 g/h is stripped, and 0.00 percent or 0.0 g/h is biodegraded.

Also, the primary sludge stream removes 9.97 percent or 1.0 g/h, anc the secondary waste sludge stream removes 9.50 percent or 0.9 g/h.

The concentration of the chemical in the air off-gas is 0.0004 g/m3. The primary sludge concentration is 0.02 g/m3; and the secondary sludge concentration is 0.02 g/m3.

The secondary effluent concentration is 0.0095 g/m3. This determines that the water pollution control plant is 24.08 percent effective for the removal of XYZ

The data sheet lists the input data, followed by a table which details the water, sludge and air concentrations, as well as the fugacity for each of the primary, aeration, and secondary tanks. The data sheet is also supplemented with a chart showing the chemical mass fluxes in each process stream.

The schematic diagram uses a "black-box" approach to symbolize each tank. The picture provides data on the volumetric flowrates of each process stream, the mass flux of the chemical in each stream, as well as the fugacity, water, air and sludge concentrations in each vessel.

The narrative summary is a one page summary of the plant flows and chemical concentrations in each phase in each tank. The summary also provides an overall statement of the fate of the chemical in the WPCP.

EXPERIMENTAL

A series of experiments were performed to obtain verification data for the model using a bench-scale completely mixed activated sludge plant. A flow diagram of the apparatus is shown in Figure 4. Where possible, glass was used to minimize adsorption of the chemicals to the walls of the vessels.

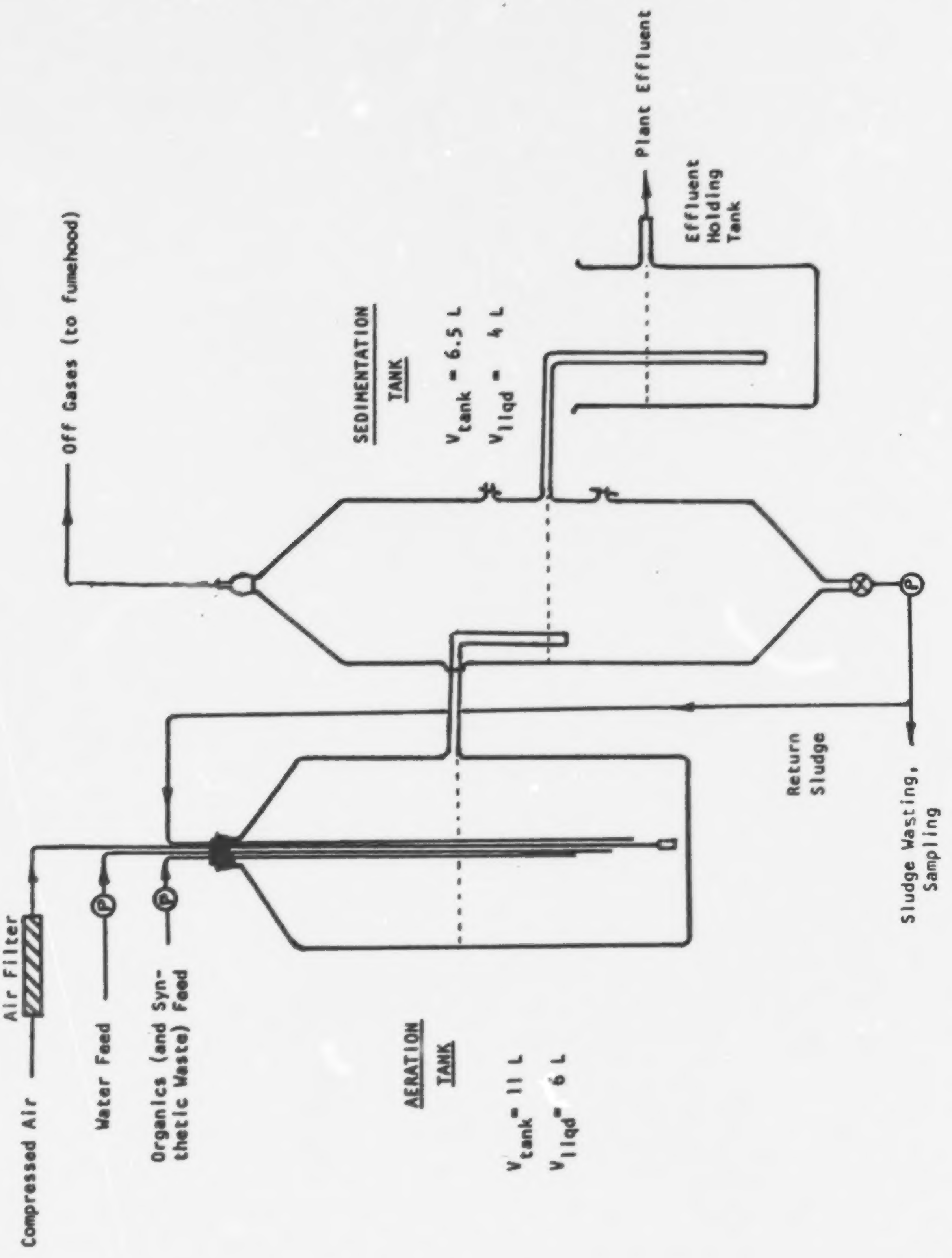
To validate the model for general use, and to cover a wide range of chemical properties (water solubility, vapor pressure, octanol-water partition coefficient and biodegradation rates),the four chemicals toluene, chlorobenzene, naphthalene and pentachlorophenol were studied.

A concentrated solution of the chemicals was prepared by dissolving each chemical in a pure methanol solution which was then injected into the aeration tank. This method of entry ensured that the chemicals were in dissolved or sorbed form, and not present as a separate phase.

Stripping studies were conducted in a pure water system without biomass in order to determine the fate of the chemical at various air (0.33 to 3 L/min), water (12.5 to 25 mL/min), return sludge (4 to 7.5 mL/min), and chemical (0.07 to 0.9 g/min) flowrates. These results were then compared to the predictions by the model .

Dead biomass, consisting of sludge autoclaved three times at 121°C and 202.7 kPa for 15 minutes, was introduced into the stripping apparatus to determine the effect of sorption on the fate of the chemicals. Air, water, and sludge samples were analyzed to determine the concentration of the chemical in each phase. These results were then compared to the model predictions.

Fig. 4: Laboratory Activated Sludge Plant



The third stage of the experiement consisted of adding active biomass into the system to study its effects on the fate of the chemicals of concern. The activated sludge used for the seeding of the reactors was obtained from a local municipal activated sludge plant. The bench-scale units were initially fed a synthetic waste comprised of peptone, beef extract and inorganic nutrients until stable operation of the activated sludge reactors was achieved. The chemicals were then added to the influent at low concentrations to allow the activated sludge to become acclimated to the chemicals. The systems were operated at a hydraulic retention time of 7 to 8 hours, with a mean cell residence time of approximately 7 days.

Water samples were analyzed by solvent extraction using hexane. The samples were analyzed on a gas chromatograph equipped with a flame ionization detector, and a stainless steel column packed with 10% SE-30 P, AW-DMCS, 60/80. The accuracy of extraction was evaluated by computing the recovery in spiked samples.

Air samples were collected by diverting a known fraction of the off-gas stream through a liquid nitrogen cooled collection trap. After approximately 1 hour sampling, the trap was removed from the Dewar flask, the contents were extracted using hexane, and the extract was analyzed by GC.

For the sorption and biodegradation experiments, the concentration of the chemical sorbed on the sludge was determined by centrifuging sludge samples, followed by Soxhlet extraction for 4 hours using hexane as the solvent. The hexane was collected and analyzed by GC.

RESULTS AND DISCUSSION

The general aim of the series of experiments was to establish a mass balance for the chemical under various treatment regimes, ranging from simple air stripping tests to a full simulation of stripping, biosorption and biodegradation. The amounts biodegraded could only be inferred by difference. It is believed that the most relevant expression of the results is as percentages by mass of the amount of chemical fed to the system, as accounted for in the various exit streams. These amounts were estimated from flowrates and concentrations. The general aim of the project is to establish a capability of predicting these percentages in full scale plants. Only a brief review of results is presented here.

The experimental and predicted mass balance concentrations for the stripping tests agreed well ,with up to 16% difference. In most cases, the overall mass balance recovery was over 96%.

In the stripping-sorption tests, the water, air, and sludge concentrations were in fair agreement with the predicted results, but there was considerable difficulty in achieving satisfactory mass balances.

The validation of the model for combined stripping-sorption-biodegradation proved to be very difficult as a result of the operational problems with the laboratory-scale activated sludge plant. However, a total of nine experiments were conducted and biodegradation rate constants estimated.

In general, it was found that with the resources and facilities available, it was exceptionally difficult to maintain a steady-state laboratory scale activated sludge plant. There were frequent interruptions due to component failure, usually at night when the systems were unsupervised. Similiar experiences have been reported by other groups and we have concluded that to obtain reliable data, it is necessary to have at least a facility and services comparable to those of the Environment Canada facility at Burlington.

Other Validation Approaches

Three other approaches to model validation or calibration are being pursued.

First, the model is being applied to data obtained from other groups, mainly in the US,for example in Oklahoma, Purdue, Cincinatti, and Michigan.

Second, the model is being compared in predictive performance to other models. This is not a validation, but it should highlight any major discrepancies.

Finally, an attempt is being made to apply the model to actual operating data from WPCPs, for example at Hamilton. Ultimately, this is the most useful data and represents an essential calibration. Because of the variable nature ofWPCPs, it is likely that laboratory simulators will never satisfactorily mimic full scale performance. If the model can be used to correlate and even predict full scale performance, it will be an invaluable tool for the rational assessment of the fate of toxic organic chemicals in WPCPs,and could thus play a useful role in regulating discharges to municipal collection systems to levels judged to be sufficiently low that, after treatment, the receiving water, air and sludge are not adversely affected by the various effluents from the plants. This is the goal of the present research effort.

CONCLUSIONS

A fugacity modelling system has been developed which can predict the phase concentrations and process stream fluxes in a wastewater treatment plant based on the properties of the chemical (molecular weight, water solubility, vapour pressure, octanol-water partition coefficient, and biodegradation rate constant) and the operating parameters of the treatment plant. The model is compatible with an IBM Personal Computer and is simple to use.

The model output correlates well with models proposed by other workers such as Blackburn (3), Roberts (4), and Kincannon and Weber (3). It predicts with reasonable accuracy the fate of organic chemicals as determined in a laboratory-scale pollution control plant. It is currently being tested using data from other laboratory and full scale systems. It is believed that the model structure is based on sound physical, chemical and biological principles, and should, when validated, be capable of adequately simulating the performance of full-scale treatment plants.

REFERENCES

1. Mackay, D., Paterson, S., "Calculating Fugacity", Environ. Sci Technol., 15(9), 1006-1014 (1981).

2. Clark, B.E., "A Predictive Fate Model for Organic Chemicals in a Water Pollution Control Plant", MASc Thesis, Dept. of Chemical Engineering, University of Toronto, (1986). Interface", Nature, 247, 181-184 (1974).

3. Blackburn, J.W., Troxler, W.L., Sayler, G.S., Breen, A., Yagi, O., "Prediction of the Fates of Organic Chemicals in Activated Sludge Wastewater Treatment Processes", Draft Publication, Contracts 68-03-3027, Work Assignments 1 and 6, 68-03-3074, Work Assignment 2, November, 1983.

4. Roberts, P.V., Dandliker, P.G., "Mass Transfer of Volatile Organic Contaminants from Aqueous Solution to the Atmosphere during Surface Aeration", Environ. Sci. Technol., 17, 484-489 (1983).

Fig. 5: Definition of "D" Values

E_W = emissions into primary tank (mol/h)

$D_{PS} = G_{PWS}Z_W + G_{PBS}Z_B$ (ie. chemical flow in raw sludge)

where G_{PWS} is water flow in raw sludge stream (m^3/h)

G_{PBS} is biomass flow in raw sludge stream (m^3/h)

Z_W is water fugacity capacity (mol/m^3. Pa)

Z_b is biomass fugacity capacity (mol/m^3. Pa)

$D_{PB} = V_{PB}k_{PB}Z_B$ or $V_{PT}k_{PT}Z_{TP}$ (ie. biodegradation in primary tank)

where V_{PB} is biomass volume in primary tank (m^3)

V_{PT} is total volume in primary tank (m^3)

V_{PW} is water volume in primary tank (m^3)

k_{PB} is rate constant for biodegradation based on concentrations in biomass (h^{-1})

k_P is rate constant for biodegradation based on total concentration in water and biomass (h^{-1})

Z_{TP} is overall fugacity capacity in primary tank defined as $(V_{PW}Z_W + V_{PB}Z_B)/V_{PT}$

k_{PT} and k_{PB} are related by $k_{PB} = k_P(1 + V_{PW}/(V_{PB}K_{BW}))$

$$= k_P\frac{(\text{total chemical present})}{\text{amount of chemical in biomass}}$$

$1/D_{PV} = (1/k_{WP}A_PZ_W) + (1/k_{AP}A_PZ_A)$ (ie. volatilization from primary tank)

where k_{WP} is water side mass transfer coefficient in primary tank (mol/h)

k_{AP} is air side mass transfer coefficient in primary tank (mol/H)

A_P is surface area of primary tank (m^2)

Fig. 5 cont.

$D_{PF} = G_{PWF}Z_W + G_{PBF}Z_B$ (ie. chemical flow from primary tank to secondary tank)

where G_{PWF} is water flow from primary to aeration tank (m^3/h)

G_{PBF} is biomass from from primary to aeration (m^3/h)

E_A = input of chemical in input air (usually zero) (mol/h)

$D_{AB} = V_{AB}k_{AB}Z_B$ or $V_{AT}k_{AT}Z_{AT}$ (ie.biodegradationinaeration tank)

variables defined similarily as for primary tank, but for aeration tank

$D_{AV} = G_AZ_A$ (ie. stripping from aeration tank)

where G_A is aeration rate, or more specifically the flow rate of air which becomes saturated with chemical (m^3/h)

$D_{AF} = G_{AWF}Z_W + G_{ABF}Z_B$ (ie. chemical flowfromaerationto secondary tank)

where G_{AWF} is water flow from aeration to secondary (m^3/h)

G_{ABF} is biomass flow from aeration to secondary (m^3/h)

$D_{SB} = V_{SB}k_{SB}Z_B$ or $V_{ST}k_{ST}Z_{ST}$

variables defined similarily as for primary tank, but for secondary tank

$1/D_{SV} = 1/(k_{WS}A_SZ_W) + 1/(k_{AS}A_SZ_A)$ (ie. volatilization from secondary tank)

variables defined as for volatilization from primary tank

$D_{SF} = G_{SWF}Z_W + G_{SBF}Z_B$ (ie. chemical in final effluent)

where G_{SWF} is water flow rate in final effluent (m^3/h)

G_{SBF} is biomass flow rate in final effluent (m^3/h)

TOXICITY OF PENTACHLORPHENOL TO ZOOPLANKTON

by

N.K. Kaushik and G. Stephenson
Department of Environmental Biology
University of Guelph
Guelph, Ontario N1G 2W1

INTRODUCTION

Approximately 3.4 million kilograms of chlorinated phenols (CP) are used annually in Canada; 80% of these are used in the form of pentachlorophenol (PCP), which is used as a wood preservative and in other activities associated with the forestry industry (Hoos, 1978).

In the U.S.A., 85% of human urine samples tested had mean concentrations of 6 ppb of PCP (cf. Cirelli, 1978). No similar study has been conducted in Canada; however, PCPs have been identified in samples of water, sediment, snow melt, agriculture produce, sewage effluent, landfill leachates and even aquatic biota (snails, fish, crayfish). Wood-preserving plants are located across the country with the highest concentration of both pressure and non-pressure treatment plants located in Ontario. An extensive survey of the Great Lakes Basin for detectable levels of PCP and of 85 whole bulk water samples collected, only 8 sites produced samples with no detectable PCP (Jones, 1981). Lake Ontario and the Bay of Quinte contained the highest concentrations (< 5 ng/L to 23,000 ng/L) (Fox and Joshi, 1984). Other designated routes of entry into the aquatic environment were on-site application of preservatives to wood products, petrochemical drilling fluids, aqueous chlorination, pulp and paper mill wastewaters, tanneries and industrial cooling systems. Despite this, almost ubiquitous distribution of PCP in the environment, there remains a paucity of scientific data regarding the fate and effects of PCP (Inglis and Davis, 1972; Adelman and Smith Jr., 1976; Mattson *et al.* 1976; Guo *et al.*, 1979) in aquatic ecosystems, which are, in many cases, the final sinks for such toxicants.

Toxicity of PCP to fish has been investigated and the effects of PCP on laboratory cultures of algae has been studied to a limited extent (Gelfaud, 1941; Palmer and Maloney, 1955; Enigk and Duwel, 1960), but comprehensive studies on the effects of PCP on freshwater zooplankton especially under Canadian conditions are limited (Jones, 1981). Secondary producers, in particular the cladoceran zooplankton, that feed primarily on phytoplankton and/or detritus are essential to transfer of energy within aquatic systems. Zooplankton are the major dietary component of planktivorous fish and the sole dietary requirement of some immature stages of fish. They are also essential to the cycling of nutrients in lakes.

Chlorinated phenols (CPs) including PCP are in Category II of Environment Canada's list of Priority Chemicals and as such are regulated by Agriculture Canada under the Pest Control Products Act. Concern regarding fate and effects of CPs and their formulated impurities in the environment has been expressed in a technical review (Jones, 1981) and changes in the regulatory status of the chlorophenols appear imminent.

With this background in mind, we initiated studies to determine toxicity of pentachlorophenol with three age classes of *Daphnia magna* and with adult *Daphnia galeata mendotae*. Our main objectives were to determine acute and chronic toxicity of pure and technical formulations of PCP to the above two species of zooplankton, to determine effects of pH and temperature on toxicity of these formulations and to determine bioaccumulation and bioconcentrations of PCP in zooplankton. The present paper describes only preliminary results dealing with some of the objectives and the investigation is still in progress.

MATERIALS AND METHODS

Acute Toxicity of Two Formulations of Pentachlorophenol

A pure formulation (99%) of pentachlorophenol was obtained from Aldrich Chemicals, Milwaukee, Wisconsin, and a technical formulation (86%) from Stanchem, Toronto, Ontario. A series of acute static toxicity tests were performed for both these formulations with three age classes (young, juvenile, and adult) of *D. magna* and with adult *D.g. mendotae*.

Test solutions were made from the stock solutions by dilution with aerated well water (pH 7.5-7.8, alkalinity 223 ± 4.8 mg/L, particulate organic carbon 1.1 ± 0.4, dissolved organic carbon 0.5 ± 0.1 mg/L). A test consisted of nine treatments - eight concentrations of PCP (0.75, 1.0, 1.5, 2.0, 2.5, 3, 4, and 5 mg/L) that encompassed a response range of 0 to 100% mortality, and controls with an acetone equivalent of the maximum PCP concentration. Each treatment had five replicate beakers with 80 mL of a given test solution and five daphnids were placed in each beaker for a total of 25 daphnids per treatment. The exposure durations of 24, 48, and 72 h occurred under controlled conditions with a photoperiod of 16 light h: 8 dark h and a constant temperature of 20 ± 1°C. The results of the acute toxicity tests were summarized by comparing the estimated LC_{50} values using analyses of variance followed by DMRT procedures (PARAMETRIC, ANOVA, DUNCAN; TERRY JAMES, UNIVERSITY OF GUELPH). Values were derived from probit analyses (PARAMETRIC, PROBIT; TERRY JAMES, UNIVERSITY OF GUELPH) using an IBM-PC.

Chronic Toxicity Tests of Two Formulations of Pentachlorophenol

A chronic toxicity study consisting of eight treatments was conducted with *D. magna*. The treatments included acetone controls, four nominal sublethal concentrations of technical PCP (0.01, 0.05, 0.1, and 0.5 mg PCP/L) and three nominal sublethal concentrations of pure PCP (0.01, 0.05 and 0.1 mg

PCP/L). There were 20 daphnids in each treatment, one daphnid per beaker with 80 mL of test solution in each beaker. Experimental conditions were comparable to those in the acute toxicity tests. The test solutions were changed every second day at which time the animals were fed 2.5 mg green algae/L. The daphnids were checked daily and twice to appearance of the primiparous instar, twice to release of first brood, number of young produced, adult mortality, the number of moults and appearance of ephippia recorded. The experiment was terminated when all of the daphnids had expired.

Interaction of Low pH and Acute Toxicity of Pentachlorophenol

Acute toxicity test procedures as described previously were repeated with *D. magna* and *D.g. mendotae*, only the pH of the well water was lowered from 7.8 to 5.5 (± 0.5) by addition of 0.1 N sulfuric acid. The pH of the test solutions in each beaker was measured every 11 h and adjusted when necessary by additions of minute quantities of sulfuric acid in order to maintain a constant pH over a 48 h period. At this time the test organism was removed temporarily from its container and we found no effect on survival of the daphnids by this additional handling. The pH was measured with a Nester pH pen.

RESULTS

Acute Toxicity of PCP

The toxicity of technical and pure PCP to daphnids was influenced by both exposure duration, age of organism and species of test organism. Young *D. magna* were equally susceptible to technical and pure PCP, whereas the juvenile and adults were less tolerant of the pure pentachlorophenol (Table 1). Pure PCP was more toxic to juveniles at 48 and 72 h exposure durations and more toxic to adults at all exposure durations (Table 1). The pure PCP was equally toxic to all age classes of *D. magna* regardless of exposure time, but *D. magna* young were less tolerant of technical PCP than were juveniles and adults (Table 2). D. magna was much more sensitive to pentachlorophenol regardless of the type of formulation than was D. galeata mendotae (Table 3).

PCP did not affect the time of appearance of the primiparous instar (Table 4) nor the time to release of the first brood (Table 5). The average number of young produced per female exposed to both technical and pure PCP was not significantly different from those in the controls (Table 6). Although the average number of broods produced per female was hgher in individuals exposed to PCP, the difference was not significant at $P \leq 0.05$ (Table 7). Also, the brood size of control individuals was not significantly higher than individuals exposed to both technical and pure pentachlorophenol (Table 8). In short, there was no effect of the various sublethal concentrations of technical and pure pentachlorophenol on the reproductive parameter of D. magna.

The sublethal concentrations of both technical and pure pentachlorophenol did not affect the longevity of D. magna as the survivorship curves were not significantly different from those in the controls (Fig. 1) with individuals surviving for an average of 103 days in the controls and 116, 114, 116 and 112 days in the technical formulation 0.01, 0.05, 0.1, 0.5 mg PCP/L, respectively. The mean survival time of daphnids exposed to pure PCP was 116, 109, and 118 days for 0.01, 0.05 and 0.1 mg PCP/L, respectively.

Influence of Low pH on Acute Toxicity of Pure and Technical PCP to Adult Daphnids

The mean 48 h LC_{50} estimates for adult D. magna exposed to technical and pure PCP at a pH of 5.5 were 0.88 and 0.58 mg PCP/L, respectively ($n = 3$). The mean 48 h LC_{50} estimates for D. magna exposed to pentachlorophenol test solutions with a pH of 7.8 were 2.79 and 1.78 mg PCP/L for technical and pure, Table 1. LC_{50} estimates (mg/L; mean ± SD for two formulations of PCP and three age classes of *D. magna*.

Age Class	PCP Formulation	Exposure Duration (h) 24	48	72
Young (24 ± 12 h)	Technical	1.84 ± 0.33	1.70 ± 0.28	1.53 ± 0.38
	Pure	1.87 ± 0.38	1.50 ± 0.19	1.37 ± 0.19
Juvenile (48-96 h)	Technical	2.98 ± 0.57	2.39 ± 0.48	2.21 ± 0.44
	Pure	2.22 ± 0.18	1.54 ± 0.15	1.15 ± 0.30
Adult	Technical	3.91 ± 1.15	2.79 ± 0.56	2.46 ± 0.39
	Pure	2.63 ± 0.44	1.78 ± 0.55	1.27 ± 0.61

LC_{50} estimates joined by a vertical line are not significantly different at $P \leq 0.05$.

Table 2. A comparison of the LC_{50} estimates (mg/L; mean ± SD) for three age classes of *D. magna* exposed to technical and pure formulations of PCP.

PCP Formulation	Age Class	Exposure Duration (h) 24	48	72
Technical	Young	1.84 ± 0.33	1.70 ± 0.28	1.53 ± 0.38
	Juvenile	2.98 ± 0.57	2.39 ± 0.48	2.21 ± 0.44
	Adult	3.91 ± 1.15	2.79 ± 0.56	2.46 ± 0.39
Pure	Young	1.87 ± 0.38	1.50 ± 0.19	1.37 ± 0.19
	Juvenile	2.22 ± 0.18	1.54 ± 0.15	1.15 ± 0.30
	Adult	2.63 ± 0.44	1.78 ± 0.55	1.27 ± 0.61

LC_{50} estimates joined by lines are not significantly different at $P \leq 0.05$.

Table 3. Mean LC_{50} estimates for adult *D.g. mendotae* exposed to two formulations of PCP.

PCP Formulation	Exposure Duration (h)	
	24	48
Technical	0.053	0.059
Pure	0.058	0.057

LC_{50} estimates joined by lines are not significantly different at $P \leq 0.05$.

Table 4. Average time of appearance of the primiparous instar in the brood chamber (days).

Criterion 1	Time (days) $\bar{x} \pm SD$
Control	7.54 ± 1.2
Technical - PCP	6.94 ± 1.3
Pure - PCP	7.12 ± 0.9

Table 5. Average time to release of the first brood in each treatment (days).

Criterion 2	Time (days) $\bar{x} \pm SD$
Control	12.86 ± 0.84
Technical - PCP	13.10 ± 1.21
Pure - PCP	12.91 ± 0.92

Table 6. Average number of young produced per female per treatment.

Criterion 3

		Concentration				
		0	0.01	0.05	0.1	0.5
Control	$\bar{x}$	285	-	-	-	-
	SD	102				
Technical PCP	$\bar{x}$	-	291	303	326	239
	SD		79	96	76	60
Pure PCP	$\bar{x}$	-	279	259	276	-
	SD		71	75	66	

Table 7. Average number of broods per female per treatment.

Criterion 4

		Concentration				
		0	0.01	0.05	0.1	0.5
Control	$\bar{x}$	24.84	-	-	-	-
	SD	8.27				
Technical PCP	$\bar{x}$	-	27.55	27.30	29.32	26.10
	SD		7.20	8.72	7.20	6.68
Pure PCP	$\bar{x}$	-	27.75	25.25	27.05	-
	SD		6.56	7.78	6.84	

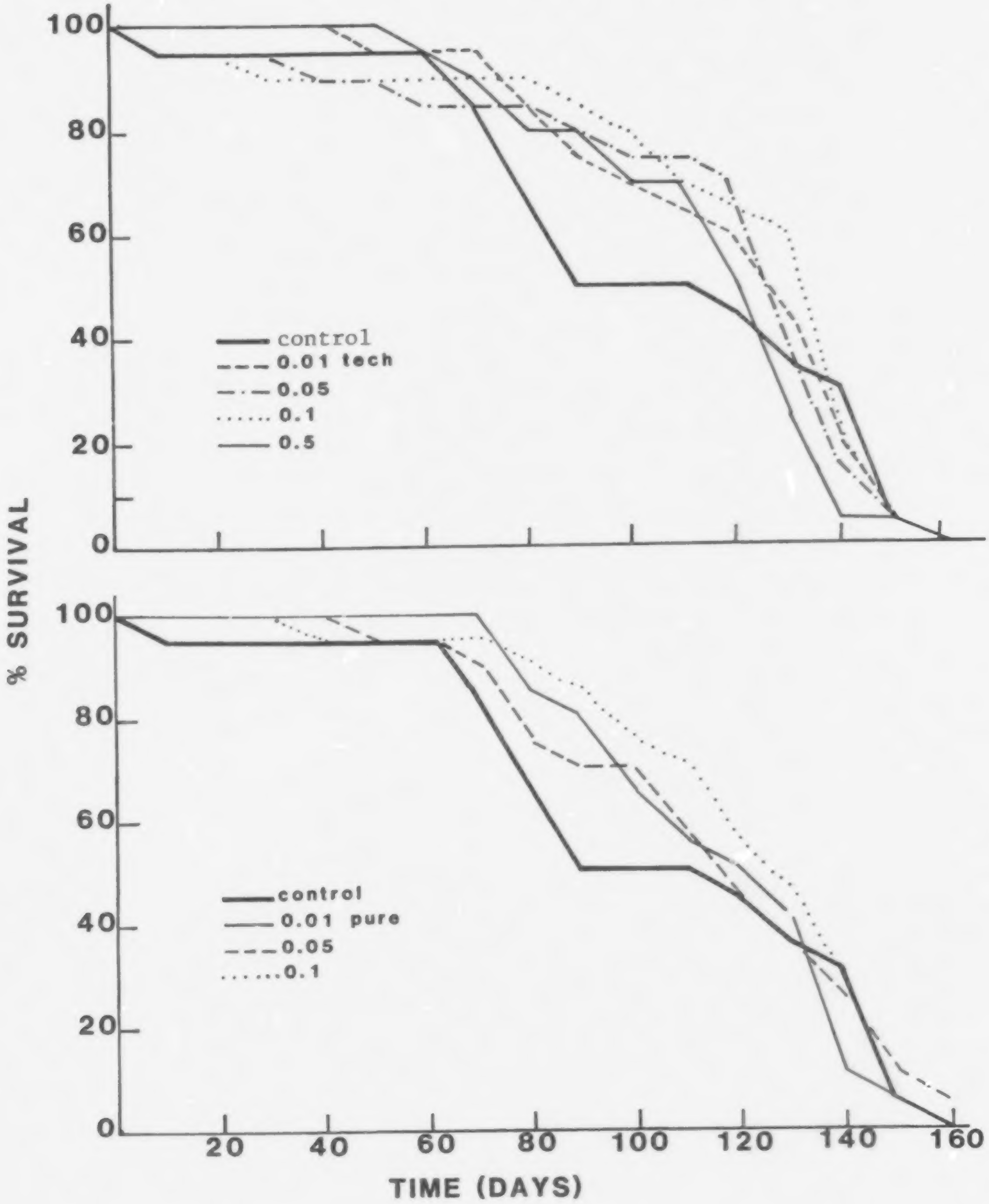


Fig. 1. Longevity of control daphnids and those exposed to technical and pure pentachlorophenol.

respectively. Thus the toxicity of both formulations of PCP appears to be more toxic at lower pH values. The trend appears to be similar for D.g. mendoate but a sample size of two is only indicative of a trend.

Table 8. Average number of young per brood per treatment (brood size).

Criterion 5		Concentration				
		0	0.01	0.05	0.1	0.5
Control	$\bar{x}$	11.29	-	-	-	-
	SD	4.39				
Technical PCP	$\bar{x}$	-	10.54	11.36	11.23	9.19
	SD		3.88	4.84	4.58	3.62
Pure PCP	$\bar{x}$	-	10.03	10.35	10.29	-
	SD		4.67	4.86	4.73	

DISCUSSION

Earlier studies, as summarized by Jones (1980), have recorded 24 LC_{50} for Daphnia magna to range from 1.1 to 2.0 and 48-h LC_{50} from 0.60 to 0.79 mg PCP/L. The values obtained in our studies for 24 to 72 h LC_{50} ranged between 1.15 to 3.91 mg/L.

Exposure of D. magna to sublethal concentrations (ranging from 10 to 500 ug/L) of technical and pure PCP did not affect longevity. However, in a recent study (Hedtke et al. 1986) with three species of Cladocera (Ceriodaphnia reticulata, Simocephalus vetulus and Ceriodaphnia affinis), although most of the concentrations used (22 to 504 ug/L) did not affect survival, concentrations higher than 119 ug/L PCP did affect survival. However, these studies were carried out at pH 7.3 whereas the pH of well-water used in our studies ranged between 7.5 to 7.8. Our preliminary studies indicate that water pH has a profound effect on toxicity and hence perhaps survival. The mean 48-h LC_{50} for adult *D. magna* at pH 7.8 for technical and pure PCP were 2.79 and 1.78 mg PCP/L, whereas corresponding values at pH 5.5 were only 0.88 and 0.58 mg PCP/L. So the effect observed by Hedtke *et al.* (1986) could be because of slightly lower pH value of water used by them. However, it is possible that the effect noticed by Hedtke *et al.* (1986) is because of the species of cladocera used. As observed with survival, Hedtke *et al.* (1986) did record significant effect on the number of young produced per female. In our studies no significant effect was observed in this regard also. These differences again could be because of the pH differences or because of different species of cladocera used as test organisms. They made no observations on the time to first brood and number of broods produced per female.

Acknowledgements

The authors are thankful to the Ontario Ministry of the Environment for financial assistance.

References

Adelman, I.R. and L.L. Smith, Jr. 1976. Fathead minnows, *Pimephales promelas* and goldfish, *Carassius auratus*, as standard fish in bioassays and their reaction to potential reference toxicants. J. Fish. Res. Brd. Canada 33: 209-214.

Cirelli, D.P. 1978. Patterns of pentachlorophenol usage in the United States of America - an overview. pp 13-18. *In*: K.R. Rao (ed.). Pentachlorophenol. Plenum Press, New York, NY.

Enigk, K. and D. Duwel. 1960. Die Durchfuhrung der Bekampfung der Leberegelschmecke *Galba truncatula* (Limnaeidae) Monatsh. Tierheik. 12: 259.

Fox, M.E. and S.R. Joshi. 1984. The fate of pentachlorophenol in the Bay of Quinte, Lake Ontario. J. Great Lakes Research 10: 190-196.

Gelfaud, M. 1941. Sodium pentachorophenate treatment on cooling water. (Water Pollut. Abst. 14) Power Plant Eng. 45: 60.

Guo, P.H.M., P.J.A. Fowlie, V.W. Cairns, and B.E. Jank. 1979. Activated sludge treatment of a wood preserving effluent containing pentachlorophenol. Wastewater Technology Centre E.P.S. Report.

Hedtke, S.F., C.W. West, K.N. Allen, T.J. Norberg-King, and D.I. Mount. 1986. Toxicity of pentachlorophenol to aquatic organisms under naturally varying and controlled environmental conditions. Env. Tox. and Chem. 5: 531-542.

Hoos, R.A.W. 1978. Patterns of pentachlorophenol usage in Canada - an overview. pp 3-13. In: K.R. Rao (ed.). Pentechlorophenol. Plenum Press, New York, NY.

Inglis, A. and E.L. Davis. 1972. Effects of water hardness on the toxicity of serval organic and inorganic herbicides to fish. U.S. Bureau Sport Fish. Wildlife Tech. Paper 67: 1-22.

Jones, P.A. 1981. Chlorophenols and their impurities in the Canadian environment. Economic and Technical Review. EPS Report 3-EC-81-2. 434 pp.

Mattson, V.R., J.W. Arthur, and C.T. Walbridge. 1976. Acute toxicity of selected organic compounds to fathead minnows. Environ. Res. Lab. U.S.E.P.A. Rept. No. EPA/600/3-76/097. PB-262 897.

Palmer, C.M. and T.E. Maloney. 1955. Preliminary screening for potential algicides. Ohio J. Sc. 55(1): 1-8.

TOWARD THE DEVELOPMENT OF A STANDARD CLAM BIOMONITORING METHODOLOGY: PRELIMINARY RESULTS

E. Creese, D. Lewis & A. Melkic
Integrated Explorations
Guelph, Ontario

Introduction

The ability of organisms to accumulate environmental contaminants such as organochlorine compounds and heavy metals, has lead to their use in biomonitoring studies. Bivalve mollusks have been used in particular, especially in saltwater environments (Phillips, 1980). The popularity of bivalves stems from the fact that they are sedentary and thus represent the habitat in which they are found. An innovation which is still not widely practiced is the introduction of uncontaminated bivalves into habitats which are under investigation. The Ontario Ministry of the Environment (MOE) has been involved in this kind of study since the work by Curry (1977/78), who pioneered the use of the freshwater clam, **Elliptio complanata**, in the MOE.

Over the past several years in Ontario, the MOE and Environment Canada have conducted many biomonitoring studies using **E. complanata**, such as for example Kauss **et alia** (1981) and Kauss (1983). Integrated Explorations has been involved with many of these, including studies in the Niagara, St. Clair and St. Mary's Rivers and in Port Hope Harbour. Due to our involvement, particularly with the implimentation of these studies in the field, a number of questions have been brought into focus.

There are two primary areas of concern. The first is the availability of clams. To date, the source of **E. complanata** has been one area of one lake (Balsam Lake in the Kawartha district). Three hundred to thirteen hundred clams of this species in the size range 6.5 to 7.2 cm have been removed for Balsam Lake each year from 1980 to 1985 inclusive. We wanted to know if this is a reliable source. How large is the population and can it absorb the effects of government biomonitoring programs? Are their other easily reached sources of **E. complanata** or perhaps other species of clam that could be used in the event that the Balsam Lake population became contaminated? It was decided that finding such populations in areas diverse in terms of water pH and hardness would also prove useful.

The second area of concern is the tolerance of clams to field methods used during biomonitoring studies. Present field methods involve transporting the clams to the monitoring area, deploying them at the required sites and processing the clams after recovering them.

No standard method of transportation has been employed to date. Clams are maintained in Balsam Lake water. Gross overheating has been avoided by introducing ice into coolers if ambient temperatures are higher than that of Balsam Lake. Oxygen levels are checked occasionally, however, this is not a standard practice. To ensure adequate oxygen levels, large amounts of water are used to transport the clams. This method of transport has been used regardless of the distance of transport. An effort has been made to deploy the clams within a 24 hours of collecting them, however logistical problems have often caused variation in this period. Effects on bioaccumulation of differences in temperature, pH or current between Balsam Lake and the monitoring sites, although these parameters are recorded, are unknown. With current deployment methods, normal clam behaviour is interfered with. Clams can not assume their normal syphoning attitude with head down half buried in subtrate. Clams in floating cages must endure very unnatural conditions. Do these deployment conditions lead to measurable effects on bioaccumulation?

Clams are usually deployed at the site in small flat rectangular galvanized steel mesh cages, as many as 17 clams per 30 cm square cage. The cages are tethered to some stationary object on shore to to allow surface recovery. SCUBA has been used on occasion if surface recovery has been unsuccessful. A mid-depth cage is often suspended from the weighted bottom cage. Depth of cage deployment has varied from 2 m to greater than 10 m.

Processing methods to this point have been quite variable. Clams are usually shucked and frozen on dry ice on site, however, for various reasons, this is often not practical. At times clams have been kept on ice after shucking on site or clams have been kept alive on ice for varying periods after recovery before shucking and freezing.

After processing, analysis of clam tissues for various contaminants has been carried out at the Rexdale laboratory of the MOE. Currently 3 to 5 clams are analysed for each biomonitoring site.

Methods

Population Surveys

Balsam Lake

An intensive survey of the clam bed at Rosedale was carried out as well as a more extensive survey of other parts of Balsam Lake.

The Rosedale clam bed was defined in this survey as in Figure 1. It encompassed an area bounded on the south by the Trent Canal system channel, on the east by the shoreline of Balsam Lake on the west by the depth at which clams could no longer be found and on the north somewhat arbitrarily.

Observations of clams were made by a diver being towed by a boat. The transect lines which were used are shown in Fiugure 2. Communications between the diver and surface personnel enabled recording of the diver's observations on a map of the study area. Since it was impossible for the diver to actually count clams as he was passing over them, a clam density code was established by preliminary sampling. This code is presented in Table 1.

Table 1. Clam Density Terminology

Description	Density Code	Mean
Abundant	3	$75/m^2$
Frequent	2	$15/m^2$
Scarce	1	$3/m^2$
Absent	0	$0/m^2$

Size distribution of **E. complanata** in this bed was also investigated. Two areas of the bed were sampled. These two areas, Site A and Site B, are shown in Figure 2. Randomly chosen sample quadrats, of 1 m^2 size, picked clean of clams. Five quadrats were chosen at site A, an area thought to be relatively unexploited and seven were sampled at site B, an area known to have been used extensivly as a source of clams for biomonitoring. For each quadrat, the number of **E. complanata** of each length were recorded.

Other areas of Balsam Lake were explored. Using the fact that **E. complanata** appeared to be restricted to depths

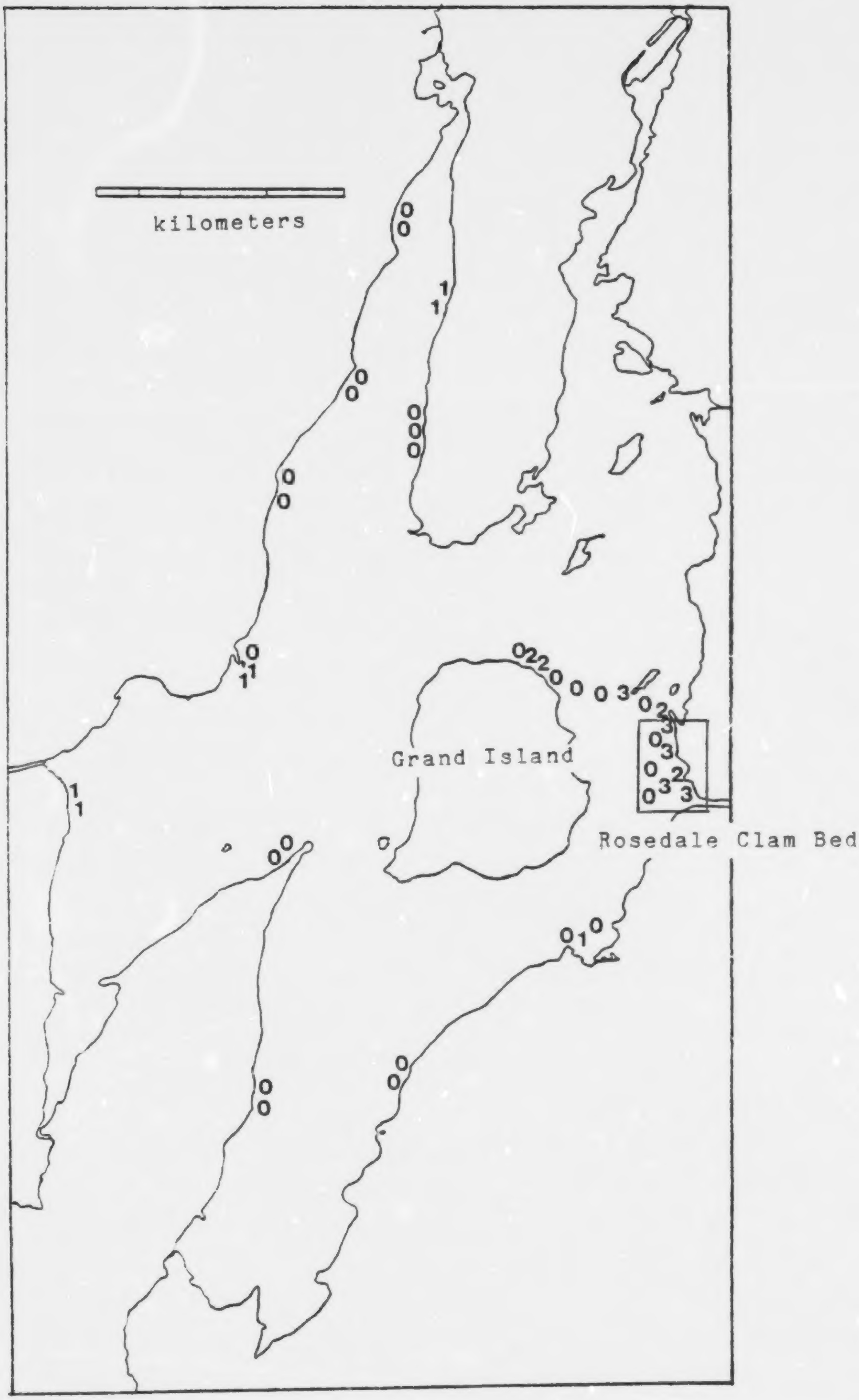


Figure 1. Map of Balsam Lake showing areas where population survey transects were run. Numbers refer to clam densities (see Table 1). The area inclosed in the rectangle is the Rosedale Clam Bed.

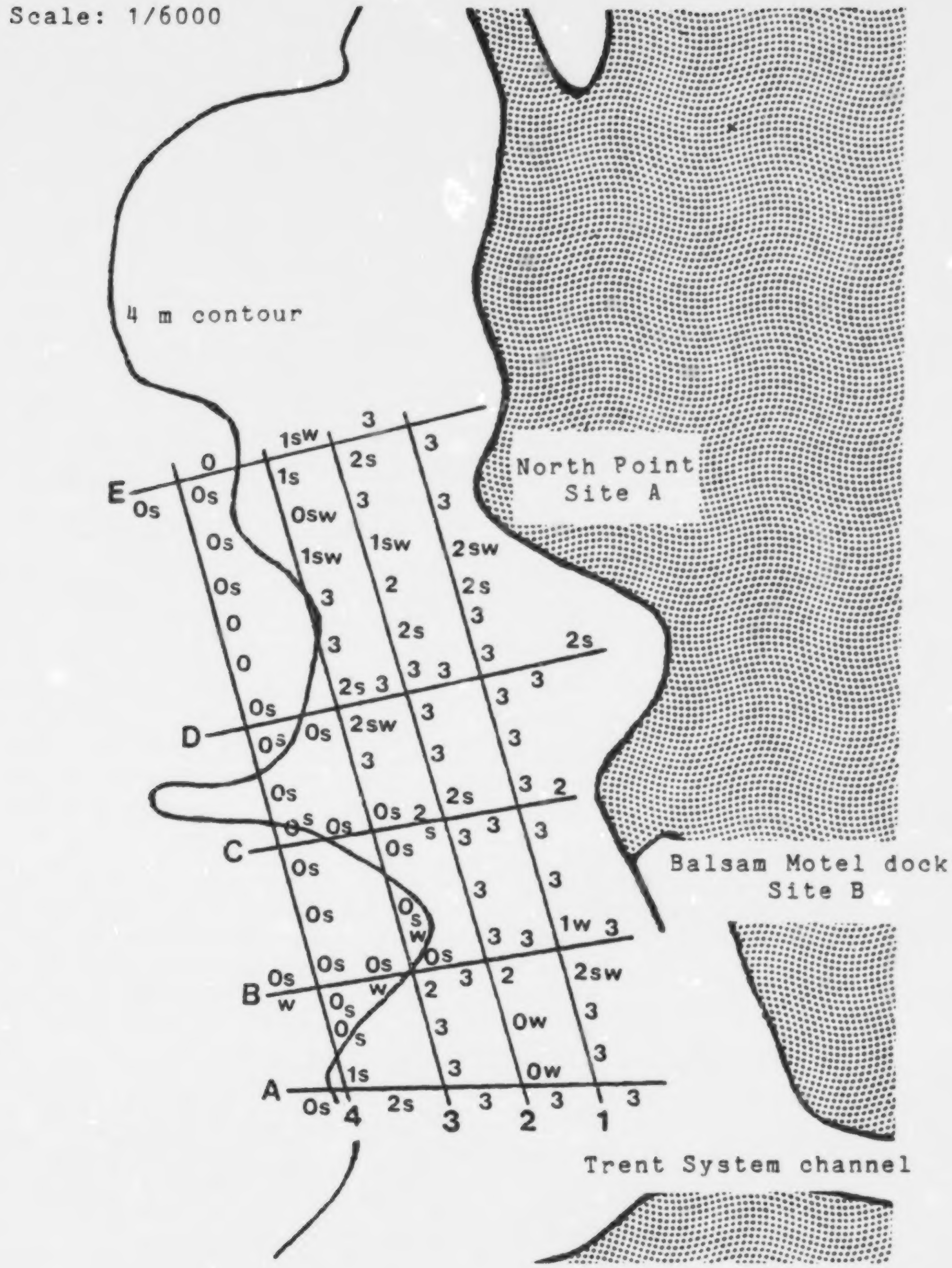


Figure 2. Map of the Rosedale Clam Bed area. The straight lines represent survey transects. Numbers are clam density codes (see Table 1). 's' indicates sand and/or silt and 'w' represents aquatic weeds.

of 4 m or less in the Rosedale clam bed, the area of exploration was similarly restricted for the most part. Transects therefore were run mostly at various places along the perimeter of the lake. One long transect that extended from the eastern shore of the lake to the northern most tip of Grand Island was also run. This transect took in a variety of substrates and included depths up to 7 m.

Other Lakes

In addition, other lakes in the area are to be investigated to find other exploitable clam populations. It was decided that finding such populations in areas diverse in terms of pH and hardness would also prove useful. Because the choice of **E. complanata** for biomonitoring seemed to be one of convenience, large populations of alternate clam species will also be noted.

As yet exploration of other lakes in the area for alternate sources of biomonitoring clams has not been carried out. This work will have been completed in November of 1986.

Experiments

The experimental part of this work has been established at a site at Niagara-on-the-Lake. The experiments have made use of Niagara River water as a source of contaminants which it is known that clams can accumulate. The experiments were concerned with the effect of various treatments on the uptake of contaminants. An examination of data on bioaccumulation in introduced clams in the Niagara River in 1980 and 1981 (Niagara River Toxics Committee, 1984) led to the conclusion that the only contaminant consistently present in concentrations above the detection limit, at Niagara-on-the-Lake, were PCB's. Therefore only differences in PCB concentrations in clams will be used in determining the effect of the various experimental treatments.

Effect of Temperature

A system was used that delivered Niagara River water into a series of temperature controlled tanks. A schematic diagram of the system is shown in Figure 3. Clams obtained from the Rosedale clam bed were exposed in a flow-through system at five temperatures, (5 C, 10 C, 15 C, 20 C and 25 C). An achievable flow rate, given the need for heating and cooling of river water for this system was 4 L/hr in each tank.

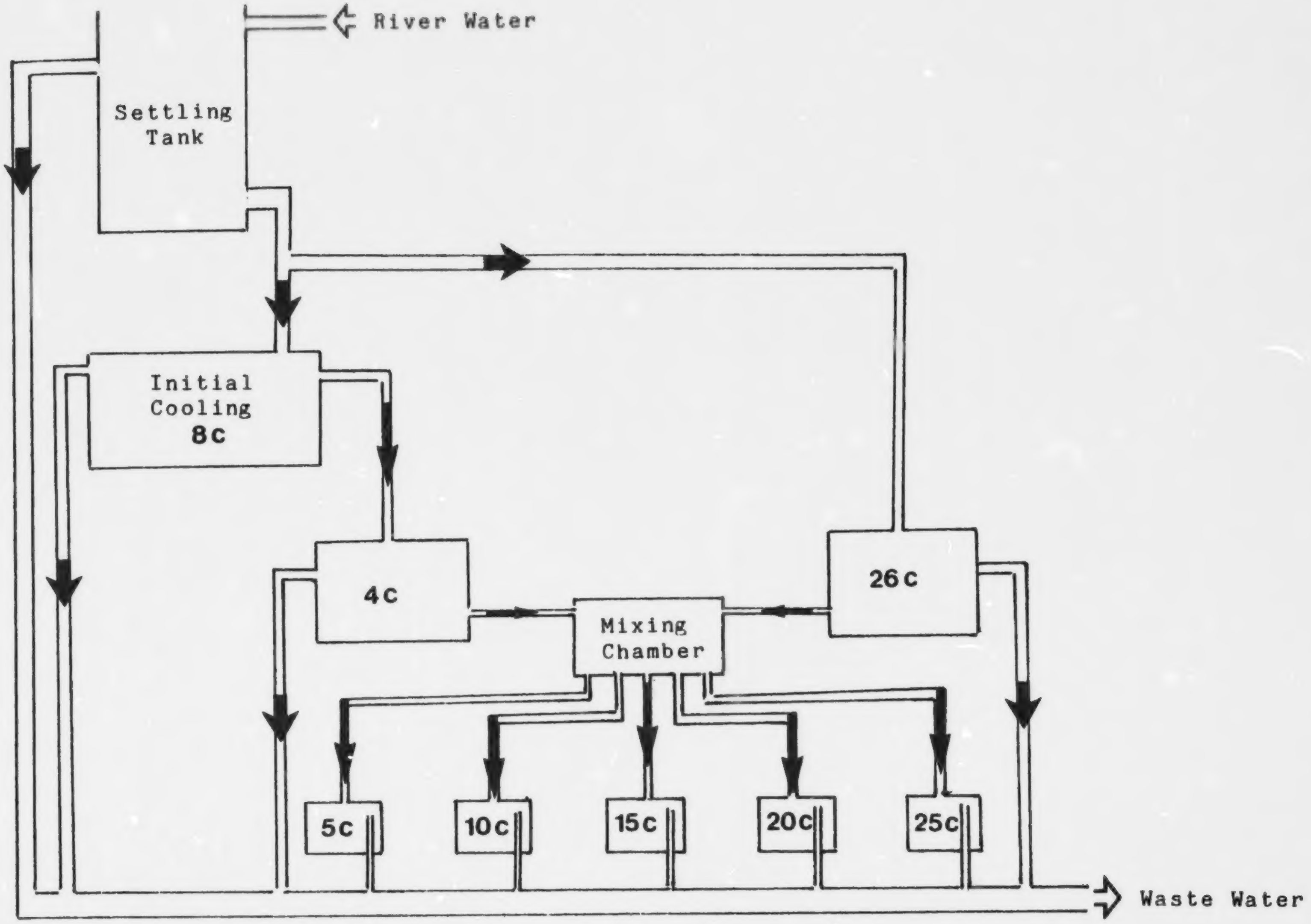


fig.3 Schematic of flow through system used in temperature test.

Prior to setting up the experiment, a check was made as to whether oxygen in incoming water would be sufficient for the needs of the clams. This was important since clams are known to reduce their filtration rates at low oxygen concentrations. For example, Badman (1974) found that **Pleurobema coccineum** had two activity regimes, one with active filtering in aerobic conditions and one with valves mostly closed in hypoxic conditions. It is likely that reduced filtration would lead to reduced bioaccumulation. The worst case was considered, one where the river water was very warm (25 C) and thus had a low oxygen concentration. It was assumed that the river water would, be saturated with oxygen since this has been noted from our past experience with the river. The saturation concentration at 25 C is 8.3 mg/L, which would give an oxygen flow rate in each of the five test aquaria, of 33 mg/hr if the incoming water was the sole source of oxygen. Each test tank contains twelve clams which would, at 20 C, use 3.0 mg/hr during sustained filtering or 4.2 mg/hr at peak oxygen consumption. These figures were arrived at using data on **Anodonta cygnea** cited by Imlay (1968). This consumption would lower the oxygen concentration from 8.3 mg/L to 7.3 mg/L. Even given some uncertainty of our estimate of clam oxygen consumption it seems unlikely that oxygen will be limiting the activity of our experimental clams even at 25 C.

Clams were exposed to this regime for a period of twenty one days, the period of time used for many biomonitoring studies. The clams were shucked immediately upon collection and frozen on dry ice. Frequent behavioural observations were made to augment chemical data.

The effect of acclimating clams to the various temperatures was also examined in this experiment by allowing half of the test clams to acclimate over a period of forty-eight hours before being exposed with the remaining clams to Niagara River water.

Effect of Biomonitoring Methods

Transport

Four transportation methods were investigated. Two methods had clams contained with large amounts of Balsam Lake water, one with the temperature controlled to equal the current temperature of Balsam Lake while the other was allowed to fluctuate with ambient temperature. In the two other treatments clams were kept moist, one was allowed to fluctuate with ambient temperature while the other was kept cool on ice. All clams were obtained from Balsam Lake and kept under these conditions for forty-eight hours before deployment in the Niagara River.

Deployment

Presently clams are deployed in flat wire cages. No attempt has been made to simulate orientation or positioning of syphoning clams observed in their natural state. Syphoning clams have been observed to orient themselves syphon up. They achieve this position either by partially burying themselves in soft sediments or by wedging themselves between small rocks. Clam abundance in our experience is usually greatest in substrates that allow either of these two activities.

To establish whether the method of containment can effect clam PCB uptake, a series of containment devices were tested. Clams were deployed in the Niagara River using five different deployment treatments on a platform constructed by SCUBA divers and located in about 3 m of water. The intake for our flow-through temperature experiment was also located on this platform.

Three of the treatments used modifications of the present clam cages. One of these used a small version of the standard clam cage where clams were crowded together with little chance of orienting themselves in an upright position. Another cage kept clams from congregating but again prevented orientation. The third cage was a floating cage which suspended the clams in individual pockets at mid-depth in the water column. The fourth device consisted of a series of support rings 2.5 in. high and 2 in. diameter which held each clam in an upright position with syphons extended beyond the upper limit of the ring. Finally, small sand filled boxes containing large 5 in. diameter rings allowed the clams to orient themselves while preventing congregation.

Each method of deployment was combined with the four transport methods giving a treatment schedule as seen in Table 2.

Processing

The clams involved in the transport and deployment experiments were shucked immediately upon collection and

	Deployment Methods				
Transport Methods	Floating Cage	Compact Cage	Modified Standard Cage	Sand Box	Support Rings
Lake Temp. Wet	6	6	6	6	6
Ambient Temp. Wet	6	6	6	6	6
Ambient Temp. Moist	6	6	6	6	6
Ice Temp. Moist	6	6	6	6	6

Table 2. Transport and Deployment Treatment Schedule for 21 day Niagara River exposure, indicating numbers of clams included for each treatment.

frozen on dry ice.

Another series of clams, deployed on the underwater platform in support rings also for 21 days were involved in a processing test. The effect of various processing methods on bioaccumulation efficiency was investigated.

Five treatments have been carried out on these clams. Two groups were held on ice, for one hour and eight hours, before being shucked and frozen. Two groups were held at ambient temperature for one and eight hours, before being shucked and frozen. The final group was shucked immediately and quickly frozen in liquid nitrogen.

A minimum of three clams will be analysed for each experimental treatment. This number is in line with methods used by MOE for their biomonitoring activities. Information obtained from Mr. Peter Kauss of the Water Resouces Branch indicates that due to variability between clams this level of analysis will allow detection of two- to three-fold differences in concentrations of PCB's.

It seems likely from the literature (Phillips, 1980) that increased precision in comparing treatments could be obtained by using lipid content of the clams as a covariate in analysis of variance. This possibility is presently being investigated.

Results and Discussion

Population Surveys

Balsam Lake

The results of the survey of the Rosedale clam bed can be seen in Figure 2. What the results indicate is that clams are abundant everywhere that the substrate consists of small stones and sand. Densities were lower when the bottom consisted solely of sand or silt especially if weeds were present. Clam densities declined rather abruptly at a depth of 4 m even on favorable substrates.

The mean densities corresponding to the density codes and the number of occurances of each code within the clam bed were used to calculate a log-mean clam density for the entire bed of approximately $23/m^2$. From navigational charts, the area of the Rosedale clam bed was calculated to be about 16 ha. The total population of the clam bed is therefore estimated to be 3.7 million.

The average loss per year due to biomonitoring activies is 850 individuals ranging from 6.5 to 7.2 cm in length. From our observations during participation in this program, all clams harvested are of breeding age. This implies an indirect loss due to reduction of recruitment. The exact size of the breeding population is not known but for the purpose of this study is taken to include all clams 6.5 cm or greater. The results of our size distribution study indicate that this gives a total breeding population of 1.3 million. Although the size of the young of the year is not known we have taken it to be not greater than 2 cm. Using these assumptions, the average direct reduction in breeding population is therefore 0.07%. Although it is likely that larger individuals will produce mor offspring than smaller individuals, we have made the conservative assumption that the annual recruitment rate will suffer a similar 0.07% reduction. Therefore the reduction in recruitment annually is estimated at 74 clams or less.

It can be seen from these calculations that the total expected population loss due to biomonitoring activities is not more than 1000 individuals per year on average. This reduction is thought to be insignificant when compared to the total population of close to 4 million. The loss is probably self-correcting due to the decrease in competition for available resources, allowing an increase on growth rate and therefore an increase in reproduction for the bed.

In other areas of Balsam Lake, the results of our survey indicate that it should not be expected to provide an alternate source of clams for biomonitoring. Population densities in other areas of the lake which were investigated proved too sparse to permit easy collection. This can be seen in Figure 1. An area immediately to the north of Grand Island had a small bed but this was not considered substantial enough to support long term biomonitoring efforts.

Experiments

Since the chemical analyses of the clam tissues are not yet completed, full experimental results can not be given.

Effect of Temperature

Observations of clams at the five test temperatures were made throughout the 21 day trial. A gradient of clam activities was observed. Clams situated in the 15 C to 25 C tanks all showed active syphoning along with foot movement. Clams were so active that support rings had to be secured to prevent movement. Clams in the 10 C test tank also showed syphoning activity, however valve or foot movement was not noticed. Clams located in the 5 C tank were least active, showing reduced syphoning, valve closure and no foot movement.

As previously mentioned, reduced syphoning may lead to reduced bioaccumulation. At this point speculation leads us to believe that levels of PCB's in clam tissues will be reduced at lower temperatures, however this remains to be seen.

Effect of Biomonitoring Methods

No results are available at the present time.

Conclusions

1) The effect of harvesting clams for biomonitoring studies from the Rosedale clam bed in Balsam Lake is insignificant.

2) Other parts of Balsam Lake should do not represent an alternate source of clams for biomonitoring, since population densities are too sparse to permit easy collecting.

3) It appears from behavioural obsevations that temperature and deplyment methods should be of concern for biomonitoring activities. More will be known when the results of the chemical analyses are available.

References

Badman, D.G. 1974. Changes in activity in a freshwater clam in response to oxygen concentration. Comp. Biochem. Physio. **47A**: 1265-1271.

Curry, C.A. 1977/78. The freshwater clam (**Elliptio complanatus**), a practical tool for monitoring water quality. Water Pollution Research Canada, **13**: 45-52.

Imlay, M.J. 1968. Environmental factors in activity rhythms of the freshwater clam Elliptio complanatus catawbensis(Lea).

The American Midland Naturalist **80**: 508-528.

Kauss, P.B. 1983. Studies of trace contaminants, nutrients, and bacteria levels in the Niagara River. Journal of Great Lakes Research, **9**: 249-273.

Kauss, P.B., Griffiths, M. and Melkic, A. 1981. Use of freshwater clams in monitoring trace contaminant source areas. Conference Proceedings, Technology Transfer Conference No. 2, pp. 371-388. Research Advisory Committee, Ministry of the Environment, Province of Ontario.

Niagara River Toxics Committee, Report of. 1984.

Phillips, D.J.H. 1980. Quantitative Aquatic Biological Indicators. their use to monitor trace metal and organochlorine pollution. Appl. Sci. Publ., London.

EVALUATION OF DATA ON THE EFFECTS OF HYDRAULIC CHARACTERISTICS AND EFFLUENT CHLORINATION ON RECEIVING WATER MICRO-ORGANISM DENSITIES

by

Dr. T.P.H. Gowda and Dr. M.D. Palmer
Gore & Storrie

Copyright© 1986 Gore & Storrie Limited

EVALUATION OF DATA ON THE EFFECTS OF HYDRAULIC CHARACTERISTICS AND EFFLUENT CHLORINATION ON RECEIVING WATER MICRO-ORGANISM DENSITIES

ABSTRACT

Measured receiving water pathogenic bacterial densities downstream of treatment plant discharges were measured for both effluent disinfection and NO disinfection. A "plug" flow model predicted the receiving water densities within 0.5 log downstream of the Ingersoll (Thames River), Grand Valley (Grand River) and Peterborough (Otonabee River) WPCPs. provided the model was applied to each site separately for the day of sampling using a bacterial decay rate of 1.0/day (20°C, base e). Effluent disinfection reduced the receiving water bacterial degradations at each site. There were no statistical correlations between pathogens and indicator bacterial densities on the Thames and Grand Rivers. Klebsiella/total coliform, Pseudomonas aeruginosa/fecal coliform and Klebsiella/fecal coliform correlations did exist on the Ontonabee River for some density ranges.

1. INTRODUCTION

Chlorine disinfection of water has been a standard and widely accepted practice since the beginning of our century. Although this method of treatment has been remarkably effective in controlling waterborne bacterial diseases, the chlorine disinfection can produce small quantities of toxic trace organics like THM and residual chlorine in a receiving water is toxic to organism like fish and plankton (water quality objective is 2 ugm/L).

The Internal Joint Commission has proposed a residual chlorine water quality objective which would require treatment plants to dechlorinate effluents or apply alternative forms of disinfection. The dechlorination process increases the cost of treatment consequently the best solution would be not to disinfect at all, or at certain times, if the die-off of pathogenic bacteria could be left to natural conditions with assurance that it could not affect public health.

In 1979 the Ontario Ministry of the Environment selected Beak Consultants Limited (BEAK) to carry out a study investigating hydraulic, water quality and atmospheric conditions which contribute to the die-off bacteria from chlorinated and non-chlorinated sewage effluents in receiving waters. The overall objectives of the study were as follows (BEAK, 1982):

1. To determine if sewage effluents significantly contribute pathogenic bacteria and indicator bacteria to their receiving streams, during periods with sewage chlorination, and without;
2. To investigate the effects of natural assimilative capacity and hydraulic characteristics of the receiving waters on the growth and/or death rates of selected micro-organisms of public health importance;
3. To determine the relationship between the incidence of pathogenic bacteria and indicator bacteria in sewage effluents and in receiving waters, both with sewage chlorination and without;
4. To investigate the feasibility of using selected pathogenic bacteria as indicators of conditions hazardous to public health in effluents and receiving waters.

Detailed field studies as well as some preliminary data analyses and interpretations were carried out by BEAK Consultants Limited during 1979-82. The BEAK studies emphasized field data gathering for meeting the above objectives. The receiving water and Water Pollution Control Plant (WPCP) sites included in the studies were as follows:

- Thames River - Ingersoll WPCP
- Grand River - Grand Valley WPCP
- Otonabee River - Peterborough WPCP
- Lake Ontario - Port Hope WPCP

All four WPCP's utilize conventional activated sludge treatment and chemical addition for nutrient reduction.

The data gathered in the BEAK study included bacteriological, chemical, hydraulic, hydrologic and meteorological characteristics from each of the four sites located in Southern Ontario. The final technical report prepared by BEAK Consultants Limited included the raw data collected in the study. The analyses which utilized somewhat simpler methods, were limited to a portion of the data gathered.

In 1982 Gore & Storrie Limited were retained by the Ontario Ministry of the Environment to carry out a follow-up study to analyze all pertinent data using acceptable mathematical methods. In following sections the objectives of the study and results obtained are presented.

2. OBJECTIVES OF THE STUDY

The objectives of the study were as follows:

1. To select mathematical models applicable to the study sites considering the dominant processes affecting bacterial transport (eg., advection, bacterial decay/regrowth, longitudinal and lateral dispersion); and to test the applicability of the selected models through comparisons of predictions with the BEAK study field data for each site.

2. To apply the selected models for determining the longitudinal and lateral distances (or travel times) with respect to the WPCP outfalls at which the total and fecal coliform densities are reduced to 1000/100 mL and 100/100 mL, respectively, for both chlorine disinfection and no-disinfection periods. The influence of seasonal change, receiving stream hydrological conditions and background bacterial concentrations are to be incorporated in this evaluation.

3. To establish the statistical relations of pathogenic bacteria concentrations in receiving streams when:

   a) Total coliform concentrations in the same water were between 100 to 1000/100 mL or fecal coliform concentrations were between 10 to 100/100 mL;

   b) Total coliform concentrations were between 1000 to 10,000/100 mL or fecal coliform concentrations between 100 to 1000/100 mL.

3. WATER QUALITY COMPLIANCE ZONES

3.1 General Approach

The selection and application of mathematical methods for the first two objectives are dependent on a number of factors. These include: (1) the ability of the models to simulate the dominant processes affecting bacterial transport in the receiving waters; (2) availability of data to determine the process parameters for the suitable models; (3) the desired level of accuracy; and (4) time-frame and other resource constraints.

In this chapter, the mathematical models suitable for the objectives 1 and 2 are outlined first by giving due consideration to the above-mentioned factors and the overall scope of the study. Then, the mathematical method applicable to each study site is outlined. The predictions are compared to the data collected by BEAK for each site. Finally, the predicted travel times at which the bacterial objectives are met, have been presented.

3.2 Description of Mathematical Methods

3.2.1 General Factors

The boundaries of bacteriological water quality compliance zones in the far field regions of rivers and lakes are dependent on the outfall characteristics, mixing of effluent in the receiving water, bacterial decay and regrowth processes, and steady/unsteady nature of the system. The models applicable to river and lake sites for defining water quality compliance zones are presented in the following subsections. These models are applicable to steady state conditions. Because of limitations imposed by time and resource constraints, and data availability, models for unsteady state conditions are not considered here.

3.2.2 Models for River Sites

All the three river sites studied by BEAK involved continuous discharge of effluents. However, the analyses presented by BEAK (1982) utilized the instantaneous discharges in an attempt to relate the effluent bacterial discharges to the observed instream bacterial data. Therefore, models applicable to both instantaneous and continuous discharge conditions are described herein.

3.2.2.1 Plug Flow Model - Continuous Discharge

If instantaneous complete mixing of effluent with the receiving water is achieved immediately below the outfall, then the one dimensional (1-D) plug flow model with first-order decay is applicable. This method has been applied to the Grand River below the Brantford WPCP (Post and Gowda, 1981). The mathematical relationships are presented below:

$$C_x = C_a \exp(-K_d X/U) \quad (1)$$

$$X_s = \frac{U}{K_d} \ln (C_a/C_s) \quad (2)$$

$$t_s = X_s/U \quad (3)$$

$$C_a = \frac{C_e Q_e + C_b Q_b}{Q_e + Q_b} \quad (4)$$

where C_e, Q_e = effluent bacterial density and flow rate, respectively

C_b, Q_b = background bacterial density and flow rate, respectively, in the river channel just above the outfall

K_d = decay rate of bacteria

U = average flow velocity in the river channel

X = distance below the outfall

C_x = concentration in the river at a distance, X, below the outfall

C_s = water quality objective

X_s = distance below the outfall at which the objective C_s, is met

t_s = travel time corresponding to X_s

The temperature dependence of K_d is expressed by the van't Hoff-Arrhenius relationship:

$$K_2 = K_1 \theta^{T_2 - T_1} \quad (5)$$

where K_1 and K_2 are the decay rates at T_1°C and T_2°C, respectively; and θ is the temperature correction factor. The streamflow dependence of U is given by the

Leopold-Maddock relation:

$$U_2 = U_1 \, (Q_2/Q_1)^{u'} \qquad (6)$$

where U_1 and U_2 denote velocities at the streamflow rates Q_1 and Q_2, respectively; and u' is an exponent determined from field data.

3.2.2.2 Two-Dimensional Model - Continuous Discharge

If there are lateral concentration gradients in the far field region of the receiving stream, then a two dimensional (2-D) model that includes transport due to lateral dispersion and first-order decay should be utilized. The models applicable to such situations are described elsewhere (Gowda, 1980, 1984a and 1984b; Post & Gowda, 1981; Smith, et al, 1983; Putz, et al, 1984; Gowda & Post, 1984). The 2-D models developed from closed form analytical solutions are simpler to use. The models include MIXCALBN and MIXAPPLN for the case of pipe outfalls, and MIXCADIF for diffuser outfall discharges. The MIXCALBN and MIXCADIF models have been calibrated and verified using field data from rivers in Ontario (Gowda, 1980 and 1984b). The MIXCALBN and MIXAPPLN models are documented in a MOE publication (Gowda, 1980). The MIXCADIF model is quite similar to MIXCALBN with minor changes in input parameters.

3.2.2.3 Models for Instantaneous and Finite-Time Discharges

The mathematical methods applicable to these cases need to consider the advection and dispersion (longitudinal and/or lateral), and decay. Mathematical models for instantaneous and finite-time release cases are available (Gore & Storrie Ltd., 1984; 1985). However, the data presented in the BEAK report are not sufficient for such modelling studies. Therefore, these models are not considered further in this study.

3.2.3 Models for Lake Site

Mathematical models for coastal regions of lakes must account for transport due to longitudinal and lateral velocities and dispersion, as well as bacterial decay rates. Some of the models utilized by the MOE are described by Hamdy (1981) and Kohli (1981).

3. MATHEMATICAL MODELLING STUDIES

The analyses of mixing zone survey studies (September, November - December 1979, February 1980 for Thames River at Ingersoll; July - August, November 1979 for Grand River at Grand Valley; June, September - October 1980 for Otonabee River at Peterborough) showed that in the majority of cases analyzed, the pluf flow model could be applied. In some cases the analyses showed that the models like MIXCALBN or MIXAPPLN would be more suitable. However, the lack of data necessary to calibrate and apply these models was the reason that the plug flow model was applied to these cases as well.

The lake study data for Lake ontario at Port Hope were incomplete and no modelling is possible.

3.1 Thames River - Ingersoll WPCP

The daily average effluent flow rates were obtained from the plant operational records. The effluent bacterial densities measured on the survey days were gathered from the BEAK report.

The streamflow rates for the survey dates were obtained from the streamflow gauging stations located on Thames River at Ingersoll (upstream from the WPCP outfall) and Middle Thames River at Thamesford located below the WPCP. The study segment of the Thames River channel was divided into twelve reaches. The boundaries of these reaches include the sampling locations established in the BEAK studies. The streamflow values for the reaches lying between the outfall and the Middle Thames River confluence were calculated by adding the effluent and the upstream flow rates. For the reaches lying below the confluence, the Middle Thames River flow rates were added to those just above the confluence.

The average widths, depths and velocities for the reaches were estimated by utilizing the cross-sectional data presented in the BEAK Report in conjunction with the corresponding flow rate values. The Leopold-Maddock equations were utilized to adjust the widths, depths and velocities for the streamflow conditions observed during the surveys. These values are somewhat approximate estimates because of the fact that the exact dates of cross-sectional surveys and corresponding streamflows are not known.

The measured bacterial densities in the river just above the Ingersoll WPCP outfall were obtained from the BEAK Report. The river water temperature values observed during each survey were also obtained from the BEAK Report.

The plug flow model was utilized for this site. Individual modelling runs were carried out for each day of survey conditions. The decay rates (K_d) of fecal and total coliform bacteria were assumed to be 1.0 and 1.0 per day at 20°C (base e), respectively, for each reach based on the values reported in the literature (Zison, et al, 1978). These rates were adjusted to the temperatures observed on each sampling day (using Equation 5), and then applied to both the river background and effluent bacterial loadings.

For a comparison of the observations and plug flow model predictions, a factor (R_L) has been utilized. The factor is defined by:

$$R_L = \log \left(\frac{X_{pred}}{X_{obs}}\right)$$

in which X denotes the FC or TC bacterial density; and the subscripts "pred" and "obs" refer to the predicted and observed values, respectively. A positive value of R_L indicates a predicted value greater than observation and vice versa; and $R_L = 0$ implies perfect agreement of the two values. The bacterial measurement techniques are imprecise; and hence, the predicted and observed values are considered to be in reasonable agreement when the difference is within one-half log cycle, i.e. $R_L < \pm 0.5$.

The bacterial densities predicted by the plug flow model, as well as the measured densities for various sampling locations, are presented in Gore & Storrie 1986 for FC and TC, respectively. The times of travel (TOT) and R_L values are also given in the tables. The predicted and measured values are in reasonable agreement in most cases ($R_L < \pm 0.5$). For FC $R_L < \pm 0.5$ in 40 of 51 cases with $C\ell_2$- on and in 36 of 54 cases with $C\ell_2$- off. For TC the numbers are 37 of 51 and 37 of 54 respectively. Generally, the discrepancies are pronounced at the first station below the outfall and on those days when the background and/or effluent densities differed by more than two log cycles. The large discrepancies at the first station may be due to incomplete mixing (the model assumed complete mixing). In general, the differences seem to be unaffected by the seasons or travel times.

The plug flow model was utilized to determine the travel times with respect to the WPCP outfall at which the FC and TC densities are reduced to 100/100 mL and 1000/100 mL, respectively. The predicted travel times (hours) are summarized in Table 1 (See Appendix). In general, these predictions indicate that:

1. The travel times with effluent chlorination are generally much lower than those without effluent chlorination.
2. The river background densities have a significant effect on the travel times at which the desired objectives can be attained. Therefore, if upstream bacterial contamination is significant, then effluent disinfection may have very little effect on the stream bacteriological quality downstream of discharge.
3. The travel times are marginally affected by seasonal changes.

3.2 Grand River - Grand Valley WPCP Studies

The effluent, as well as river flow and quality data required for the plug flow model, were obtained from the plant operational data, streamflow records and the BEAK report. The decay rates for FC and TC bacteria were the same as for the Thames River studies (i.e., 1.0 and 1.0 per day) and were adjusted to the temperatures observed in the Grand River.

The observed and predicted FC and TC densities for various sampling runs are summarized in Gore & Storrie, 1986. As in the Thames River case, the predictions compare fairly well for some of the sampling runs and differ for others. For FC R_L is $< \pm 0.5$ in all cases (both for $C\ell_2$ on and off). For TC R_L is $< \pm 0.5$ in 34 of 36 cases with $C\ell_2$- on and in 25 of 36 cases with $C\ell_2$- off. The differences between the observations and predictions are seen to be quite significant for the days when the upstream densities are considerably different from the other sampling days.

The travel times at which the FC and TC densities are reduced to the guideline values of 100/100 mL and 1000/100 mL, respectively, are presented in Table 2. These predictions by the plug flow model are seen to be lower with effluent chlorination compared to the non-chlorination runs. The observed changes in background densities from one day to another are seen to affect the travel time values. The findings herein are somewhat similar to the Thames River results.

3.3 Otonabee River - Peterborough WPCP Studies

The WPCP effluent quality and flow rates, as well as the Otonabee River characteristics, were determined from various sources as for the Thames and Grand River Studies. The bacterial decay rates were also the same as in the other river studies, scaled up to the average river temperatures for each sampling day.

The FC and TC densities predicted by the plug flow model for the Otonabee River sampling sites are presented in Gore & Storrie, (1986) along with the corresponding observed values. The predictions are closer to the observations for some sampling runs, but differ in others, as for the other two river study sites. For FC R_L is <± 0.5 in 24 of 30 cases with $C\ell_2$- on and in 18 of 29 cases with $C\ell_2$- off. The numbers for TC are 23 of 30 and 24 of 30 respectively. The observed background densities on different sampling dates affect the comparative results at this river site as well.

The plug flow model predictions of travel times at which the FC and TC densities are reduced to the guideline values have been summarized in Table 3. The trends of these travel times are generally similar to those of the Thames and Grand River values.

3.4 Sensitivity of Background Bacterial Densities

The model predictions for various river sites, presented in the previous section, indicated the significance of the background levels on the times of travel at which the water quality objectives are met. The analyses for each site were both without and with background bacterial densities. In order to further evaluate the sensitivity of the background levels, additional plug flow modelling studies were carried out for the Grand River site by assuming the following levels for the summer runs:

Background FC = 100/100 mL
Background TC = 1000/100 mL

These background levels are the same as the provincial water quality objectives (PWQO). The effluent densities, decay rates and other input parameters for the model were the same as those observed during the summer 1979 Cl_2-ON (August 4 to 6) and Cl_2-OFF (August 12 to 14) studies.

The predicted travel times below the outfall at which the FC and TC bacterial objectives can be met, are summarized in Table 4. A comparison of these travel times with the corresponding values (predicted with the observed background levels) indicates that the maintenance of background levels at or lower than the PWQO will result in significant reductions in the travel times (particularly for the disinfected case) within which PWQO cannot be met. These sensitivity run predictions indicate that efforts should be directed at maintaining background bacterial densities at or below the PWQO levels.

3.5 Discussion

The discrepancies between the observations and predictions are in part caused by field sampling methodology, imprecise analytical measurement techniques, effects of ambient environmental factors, etc. Attempts were made to qualitatively assess the possible effects of sediment characteristics, hydraulic parameters and inorganic water quality parameters on the modelling results by utilizing the data presented in the BEAK report. An examination of the pertinent data for the successive reaches from each river site did not reveal any clearly identifiable factors to explain the discrepancies. However, the empirical method of using an error range (defined by the ratio $R_L < \pm 0.5$) to include most errors.

The plug flow model predictions compared reasonably well with observations with a few exceptions for each site. The assumed decay rates for FC and TC were satisfactory. Since all the river sites consist of shallow reaches, the assumed decay rates appear to be valid for the river reaches studied herein. These rates could be used for preliminary planning studies. However, their validity to a given site should be checked with the aid of field data and modelling studies.

4. STATISTICAL ANALYSIS

The total coliform (TC) and fecal coliform (FC) density data were correlated with Pseudomonas aeruginosa (PA) and Klebsiella (K). In the Beak report, the log (TC) and log (FC) were correlated with the log (PA) and log (K); however, the correlations were statistically not significant. These statistical correlations were repeated but the data were separated into groups for the river sites, namely, the Grand, Thames and Otonabee Rivers. The statistical results are summarized in Table 5. For the Otonabee River, K with TC greater than 1000/100 mL and K with FC greater than 100/100 mL have correlation coefficients of 0.78 and 0.79, respectively. The correlation coefficients are not statistically significant for all other cases.

To determine whether better statistical correlations could be obtained, the data sets were partitioned. There is a low value bias of 4 counts/100 mL for PA in the data sets; consequently, a new data set was created, omitting all PA densities of 4 or less. It is also known that the FC density evaluation is imprecise. Data from the Eastern Beaches (Toronto waterfront) indicated a precision of log (var) equal to 0.54 (N=1121) and the MOE data have indicated a precision of log (var) equal to 0.7 for Lake Ontario (Gore & Storrie Limited, 1985). The 1986 data for Western Beaches had even greater values of log (var) varied between 0.97 (N=1270) and 1.09 (N=686) for the samples taken inside and outside of breakwater respectively. Furthermore, the present guidelines for FC for receiving waters are that the geometric mean of 10 samples should not exceed 100/100 mL. The following table shows the upper limits for the FC geometric mean of 100/100 mL based on sample size, assuming a normally distributed population (U.S. Federal Register 49 (102); 21987, 24 May, 1984):

NO. OF SAMPLES	LOG (VAR) = 0.54	LOG (VAR) = 0.7
1	778	1429
2	427	655
5	250	329
10	191	232

The bacteriological sampling in the BEAK study involved one sample at each station. Therefore, instead of the interval 10 to 100/100 mL and 101 to 1000/100 mL for FC densities, the intervals of 0 to 777/100 mL and 778 to 7000/100 mL were used assuming a precision of log (var) = 0.54. The results of the statistical fitting of this data set are presented in Table 6. This partitioning of the data set did not improve the statistical fitting for the Grand and Thames Rivers, however, it did produce statistically significant relationships for PA/FC for the Otonabee River data.

Tables 5 and 6 show that the correlations between TC/FC with PA/K are generally statistically not significant for the data sets, except for the Otonabee River data which has the following relationships:

OTONOBEE RIVER

1.	TC = 1001 to 10,000/100 mL	$\log(K) = -3.48 + 0.6 \log(TC)$
2.	FC = 10 to 777/100 mL	$\log(PA) = 1.34 - 0.2 \log(FC)$ $\log(K) = 0.68 + 0.57 \log(FC)$
3.	FC = 778 to 7000/100 mL	$\log(PA) = -1.45 - 0.74 \log(FC)$ $\log(K) = 0.19 + 0.82 \log(FC)$

5. SUMMARY AND CONCLUSIONS

Data related to bacteriological impact of effluent discharges to water bodies were analyzed. The studies were conducted by BEAK Consultants Limited during 1979-82 at the following sites:

- Thames River - Ingersoll WPCP
- Grand River - Grand Valley WPCP
- Otonabee River - Peterborough WPCP
- Lake Ontario at Port Hope WPCP

The data review and analyses focussed on the following objectives:

1. Determination of longitudinal and lateral distances (or travel times) with respect to the WPCP outfalls at which the fecal and total coliform densities are reduced to 100/100 mL and 1000/100 mL respectively, for both chlorine disinfection and no-disinfection periods.

2. Establishment of statistical relationships distributions of pathogenic bacteria concentrations in receiving streams when:

    a) Total coliform concentrations in the same water were between 100 to 1000/100 mL or fecal coliform concentrations were between 10 to 100/100 mL; and

    b) Total coliform concentrations were between 1000 to 10,000/100 mL or fecal coliform concentrations between 100 to 1000/100/mL.

The suitability of data presented in the BEAK Report for applying the state-of-the-art models to each site was evaluated. It was found that 2-D models (capable of simulating transport due to lateral dispersion, longitudinal convection and decay) could not be utilized because data were not available. The lake study data were also insufficient for modelling.

The plug flow model was the most suitable model for the three river site analyses. The model was applied for each day of sampling, since the effluent and background loadings were different on each day. The bacterial decay rate was assumed to be 1.0/day (20° C, base e) for both TC and FC.

The plug flow model generally predicted observations within one half log cycle. The largest discrepancies occurred on days when the background levels differed significantly from the other days' values at the first station below the outfall. This was the case for each site. The travel times at which the TC and FC densities are reduced to the guideline limits (stated in the first objective) were smaller with effluent disinfection at each site compared to the non-disinfected cases. The background densities of FC and TC affect the travel time computations.

Statistical correlation analyses of pathogen and indicator bacterial densities were carried out. No correlation relationships could be found for the Thames and Grand River data. Only the Otonabee River bacterial data showed correlations between: (a) Klebsiella and TC; (b) P.aeruginosa and FC; and (c) Klebsiella and FC. These relationships are established for the ranges TC = 1001 to 10,000/100 mL, FC = 10 to 777/100 mL and FC = 778 to 7000/100 mL in order to account for imprecise evaluations of the bacterial densities.

REFERENCES

Beak Consultants Ltd., 1982. Bacteria in Sewage Effluents - The Effects of Hydraulic Characteristics and Effluent Chlorination on the Incidence of Micro-Organisms of Public Health Significance in Receiving Waters. Technical report prepared for the Ministry of the Environment, Toronto, Ontario.

Gore & Storrie Limited, 1986. Evaluation of Data on the Effects of Hydraulic Characteristics and Effluent Chlorination on the Incidence of Micro-organisms of Public Health Significance in Receiving Waters. Technical report prepared for the Ontario Ministry of the Environment.

Gore & Storrie Limited, 1985. Eastern Beaches Study - 1984. Technical report prepared for the City of Toronto.

Gore & Storrie Limited, 1984. Ottawa River Nuclear Spill Contingency Model Development. Technical Report prepared for the Ontario Ministry of the Environment, Toronto.

Gowda, T.P.H., 1980. Stream Tube Model for Water Quality Prediction in Mixing Zones of Shallow Rivers. Water Resources Paper 14, Water Resources Branch, Ministry of the Environment, Toronto, Ontario, Canada. 141 p.

Gowda, T.P.H., 1984a. Critical Point Method for Mixing Zones in Rivers. J. Environmental Engineering, Amer. Soc. Civ. Eng. 110 (1): 244 - 262.

Gowda, T.P.H., 1984b. Water Quality Prediction in Mixing Zones of Rivers. J. Environmental Engineering, Amer. Soc. Civ. Eng. 110 (4): 751-769.

Gowda, T.P.H. and Post, L.E., 1984. Mixing Zone Studies in the Grand River Basin. Canadian Journal of Civil Engineering 11 (2): 204-216.

Hamdy, Y., 1981. Dispersion of Effluent Plumes from Diffusers on Near-Shore Regions of the Great Lakes. Vol. I - Initial Mixing Processes. Great Lakes Section, Water Resources Branch, Ministry of the Environment, Toronto.

Kohli, B., 1981. Dispersion of Effluent Plumes from Diffusers on Near-Shore Regions of the Great Lakes. Vol. II - Surface Dilution. Great Lakes Section, Water Resources Branch, Ministry of the Environment, Toronto.

Post, L.E. and Gowda, T.P.H., 1981. Effluent Mixing Zone Studies. Grand River Basin Water Management Study - Technical Report No. 29, Water Resources Branch, Ontario Ministry of the Environment, Toronto.

Putz , G., et al, 1984. Micro-organism Survival in an Ice-Covered River. Canadian Journal of Civil Engineering 11 (2): 177-186.

Smith, D.W., et al, 1983. Effluent Mixing in Northern Rivers - The Bank Discharge. Paper presented at the Chemical Institute of Canada Conference, Calgary, June 1983.

Zison, S.W., et al, 1978. Rates, Constants and Kinetic Formulations in Surface Water Quality Modelling. Tetra Tech., Inc., Lafayette, California. Technical report prepared for the U.S.E.P.A. 317 p.

APPENDIX - TABLES

Table 1

SUMMARY OF PREDICTED TRAVEL TIMES WHERE BACTERIAL OBJECTIVES ARE MET - THAMES RIVER

SEASON & DATE	CASE	TRAVEL TIME (HRS) WHERE FC OBJECTIVE = 100/100 mL		TRAVEL TIME (HRS) WHERE TC OBJECTIVE = 1000/100 mL		UPSTREAM RIVER DISCHARGE (m^3/s)
		Without Background	With Background	Without Background	With Background	
Summer						
Sept. 6-8, 1979	Cl_2-ON:					
	Day 1	20.08	88.43	1.72	25.00	1.75
	Day 2	0.0	94.71	0.0	128.89	1.71
	Day 3	0.0	138.35	0.0	115.56	1.67
Sept. 19-21, 1979	Cl_2-OFF:					
	Day 4	200.96	202.13	142.15	148.03	1.85
	Day 5	158.58	163.09	142.37	149.99	1.76
	Day 6	158.41	158.86	216.99	217.47	1.87
Fall						
Nov.30 - Dec.2 1979	CL_2-ON:					
	Day 1	0.00	76.85	0.0	81.07	3.05
	Day 2	4.46	83.84	30.89	103.92	2.15
	Day 3	44.74	76.99	0.0	97.98	1.63
Dec. 10-12 1979	Cl_2-OFF:					
	Day 4	14.16	68.30	27.50	125.14	5.41
	Day 5	4.84	92.40	0.14	123.53	4.96
	Day 6	0.0	103.32	1.09	99.89	4.86
Winter						
Feb. 7-9 1980	Cl_2-ON:					
	Day 1	0.0	89.24	0.0	96.50	2.15
	Day 2	0.0	77.44	0.0	86.30	2.12
	Day 3	0.0	58.78	0.0	45.65	2.08
Feb. 19-21 1981	Cl_2-OFF:					
	Day 4	130.32	137.74	138.69	140.50	1.90
	Day 5	111.48	122.97	129.46	133.42	1.90
	Day 6	87.36	137.92	115.63	127.75	2.50

Table 2

SUMMARY OF PREDICTED TRAVEL TIMES WHERE BACTERIAL OBJECTIVES ARE MET - GRAND RIVER

SEASON & DATE	CASE	TRAVEL TIME (HRS) WHERE FC OBJECTIVE = 100/100 mL		TRAVEL TIME (HRS) WHERE TC OBJECTIVE = 1000/100 mL		UPSTREAM RIVER DISCHARGE (m^3/s)
		Without Background	With Background	Without Background	With Background	
Summer						
August 4-6, 1979	Cl_2-ON:					
	Day 1	0.0	29.1	0.0	59.7	0.5667
	Day 2	0.0	25.5	0.0	59.9	0.5306
	Day 3	0.0	0.0	0.0	44.6	0.4697
August 12-14, 1979	Cl_2-OFF:					
	Day 1	21.2	50.5	0.0	49.9	0.7398
	Day 2	28.3	48.6	0.0	48.5	0.6817
	Day 3	29.1	44.7	0.0	112.3	0.7449
Fall						
Nov. 5-7, 1979	CL_2-ON:					
	Day 1	0.0	0.0	0.0	3.6	3.7575
	Day 2	0.0	0.0	0.0	0.0	3.0578
	Day 3	0.0	36.2	0.0	0.0	3.0573
Dec. 16-18, 1979	Cl_2-OFF:					
	Day 1	0.0	86.5	0.0	11.4	3.1377
	Day 2	0.0	3.5	0.0	42.9	3.0477
	Day 3	0.0	17.1	0.0	0.0	3.3075

Table 3

SUMMARY OF PREDICTED TRAVEL TIMES WHERE BACTERIAL OBJECTIVES ARE MET - OTONABEE RIVER

SEASON & DATE	CASE	TRAVEL TIME (HRS) WHERE FC OBJECTIVE = 100/100 mL		TRAVEL TIME (HRS) WHERE TC OBJECTIVE = 1000/100 mL		UPSTREAM RIVER DISCHARGE (m^3/s)
		Without Background	With Background	Without Background	With Background	
Summer						
June 5-7, 1980	Cl_2-ON:					
	Day 1	0.0	14.6	0.0	22.0	37.90
	Day 2	0.0	30.9	0.0	20.2	21.20
	Day 3	0.0	4.6	0.0	28.7	21.10
June 16-18, 1980	Cl_2-OFF:					
	Day 1	112.6	112.9	87.8	90.0	23.00
	Day 2	78.9	80.3	63.7	65.6	20.30
	Day 3	104.1	104.9	89.1	89.5	23.50
Fall						
Sept. 30 - Oct. 2, 1980	CL_2-ON:					
	Day 1	0.0	3.0	0.0	2.5	34.10
	Day 2	0.0	7.0	0.0	0.0	34.50
	Day 3	0.0	0.0	0.0	0.0	39.00
Oct. 14-16, 1980	Cl_2-OFF:					
	Day 1	92.2	92.8	10.1	27.5	46.80
	Day 2	50.0	51.8	41.8	53.2	46.60
	Day 3	33.4	42.6	19.0	36.9	50.40

Table 4

SENSITIVITY OF BACKGROUND LEVELS ON PREDICTED TRAVEL TIMES GRAND RIVER

SEASON & DATE	CASE	TRAVEL TIME (HRS) WHERE OBJECTIVES ARE MET With FC Background = 100/100 mL	With TC Background = 1000/100 mL
Summer			
August 4-6, 1979	Cl_2-ON:		
	Day 1	0.03	0.08
	Day 2	0.0	0.0
	Day 3	0.0	0.0
August 12-14, 1979	Cl_2-OFF:		
	Day 1	28.6	13.3
	Day 2	34.0	13.8
	Day 3	34.6	9.6

Table 5

	TOTAL COLIFORMS (Counts/100 mL)		FECAL COLIFORMS (Counts/100 mL)	
	100 to 1000	1001 to 10000	10 to 100	101 to 1000
PSEUDOMONAS AERUGINOSA				
Grand River				
Number of readings	21	41	25	57
Intercept	0.63	- 1.60	0.55	- 0.19
Slope	- 0.0056	0.72	0.18	0.42
Correlation coefficient	- 0.0042	0.40	0.08	0.25
Thames River				
Number of readings	2	57	2	81
Intercept	--	1.79	--	- 0.02
Slope	--	- 0.21	--	0.37
Correlation coefficient	--	- 0.14	--	0.19
Otonabee River				
Number of readings	17	64	28	44
Intercept	- 0.74	- 1.18	0.60	- 0.15
Slope	0.38	0.45	- 0.20	0.21
Correlation coefficient	0.20	0.40	- 0.15	0.24
KLEBSIELLA				
Grand River				
Number of readings	30	52	32	64
Intercept	1.62	2.95	1.81	2.35
Slope	0.20	- 0.23	0.14	- 0.10
Correlation coefficient	0.11	- 0.21	0.11	- 0.09
Thames River				
Number of readings	5	61	5	89
Intercept	2.15	2.40	0.28	1.01
Slope	0.12	0.01	1.03	0.51
Correlation coefficient	0.04	0.01	0.54	0.27
Otonabee River				
Number of readings	20	44	33	26
Intercept	0.40	- 3.48	1.11	- 0.33
Slope	0.47	0.61	0.32	0.99
Correlation coefficient	0.29	0.78	0.20	0.79

Slope assumes TC/FC are independent variables.
Correlation coefficient assumes both TC/FC and PA/K are dependent variables.

Table 6

	FECAL COLIFORMS	
	10 to 777	778 to 7000
GRAND RIVER		
Pseudomonas aeruginosa		
Number or readings	24	16
Intercept	1.05	1.78
Slope	0.19	- 0.13
Correlation coefficient	0.17	- 0.09
Klebsiella		
Number of readings	86	29
Intercept	1.98	- 1.05
Slope	0.05	1.05
Correlation coefficient	0.05	0.63
THAMES RIVER		
Pseudomonas Aeruginosa		
Number of readings	49	56
Intercept	0.78	- 0.19
Slope	0.11	0.48
Correlation coefficient	0.08	0.28
Klebsiella		
Number of readings	77	67
Intercept	1.06	2.17
Slope	0.48	0.11
Correlation coefficient	0.37	0.06
OTONABEE RIVER		
Pseudomonas aeruginosa		
Number of readings	7	25
Intercept	1.34	- 1.45
Slope	- 0.20	0.74
Correlation coefficient	- 0.87	0.83
Klebsiella		
Number of readings	54	16
Intercept	0.68	0.19
Slope	0.57	0.82
Correlation coefficient	0.56	0.88

Listowel Artificial Marsh Treatment Project

J. Herskowitz, S. Black, W. Lewandowski[1]

Abstract

Five separate cattail (Typha spp.) marsh treatment systems, occupying a total area of 8670 m^2, were operated for four years. Several different marsh designs and two pre-treatment types, namely, complete-mix aeration cell effluent and lagoon effluent from the existing Town of Listowel sewage works, were tested. Marsh effluent quality achieved was at levels between conventional secondary and tertiary treatment. The marsh systems demonstrated large reductions in BOD and suspended solids on a year-round basis. Elevated ammonia, hydrogen sulphide and phenol levels in the marsh effluent in summer and/or winter months were primarily attributed to anaerobic conditions, although low temperatures appeared to be a factor in decreased ammonia removal in winter. The observed decline in annual phosphorus retention suggests progressive saturation of the phosphorus adsorption capacity of the sediment. Large reductions in fecal bacteria were achieved although in some months levels exceeded Ministry objectives for disinfected effluent. Pilot study recommendations for marsh system design and operation have been implemented at a full-scale marsh treatment facility currently operated in Port Perry, Ontario.

Key words: wetlands, cattails, Typha, wastewater, municipal sewage.

Introduction

The study of marsh wastewater treatment systems was initiated by the Ontario Ministry of the Environment in response to reports that they may provide a viable and cost-effective alternative to conventional practices of wastewater treatment in rural communities and small urban centres. Many communities in Ontario use seasonal or annual retention lagoons which must be large enough to retain the wastewater until there is adequate dilution in the receiving waters to meet Ministry water quality guidelines (MOE, 1984). Marsh treatment has the advantages of being less land consumptive than seasonal or annual retention lagoons and more economical and energy efficient than mechanical systems.

---

[1] Water Resources Branch, Ontario Ministry of Environment, 135 St. Clair Ave. W., Toronto, Ontario, Canada M4V 1P5

The primary objectives of the Listowel Artificial Marsh Project were 1) to investigate the efficiency and feasibility of year-round marshland wastewater treatment in cold climates and 2) to provide guidelines for the design and operation of marsh systems in Ontario. This paper describes the operating conditions and effluent quality achieved in Systems 3 and 4, channelized marshes used to treat lagoon effluent and aeration cell effluent, respectively, as the channelled design yielded the highest treatment efficiencies.

Description of Site and Facilities

The experimental facility was constructed adjacent to the existing 1.2 MIGD sewage works in the Town of Listowel and was operated from 1980 to 1984. A food processing plant with poultry handling facilities contributed 60-70% of the total sewage volume and BOD loadings. The existing sewage treatment at Listowel consisted of alum injection prior to a complete-mix aeration cell (3.5 day HDT) followed by two wastewater stabilization lagoons operated in series (combined retention 85 days). Alum treatment was withheld during the first two summers (May-Oct., 1981 and 1982) as the town spray irrigated an adjoining property in summer. The five separate experimental marsh systems treated 4% of the town's sewage. Wastewater was diverted from two stages of the existing system and distributed to the marsh systems as shown in Figure 1.

The marsh system designs included a channelized marsh with serpentine configuration (Systems 3 and 4), a shallow marsh (Systems 2 and 5) and a complex of shallow marsh, deep pond and channelized marsh (System 1). The channels, separated by earthen berms, were 4 m wide and 334 m long (length width ratio 17:1 in each channel). Surface areas of Systems 1 through 5 were 4172, 909, 1324, 1324 and 941 m^2, respectively. The marsh basins were composed of compacted clay and filled to a depth of 15 cm with a combination of top soil and peat (10% by volume). Cattails (predominantly *Typha latifolia* with some *T. angustifolia* present), propagated from rhizomes planted at 1 m intervals, provided a complete cover which was maintained throughout the study. The pilot project has been described in more detail in earlier reports (Wile et al, 1981; Black, 1983; Wile et al, 1985; Reed et al, 1985; Herskowitz, 1986).

Operational Conditions and Procedures

Wastewater from the existing lagoon and aeration cell was pumped to two flow splitting boxes and was then fed by gravity to the marsh systems. Inflows and outflows monitored by 30° v-notch weirs and water level recorders were used to calculate mass balances of wastewater constituents and treatment efficiencies. Due to computations indicating an excess of total hydrological input over output in some months (attributed to an underestimate of outflow discharge), monthly mass balances were adjusted accordingly to avoid overestimating treatment efficiencies.

Average hydraulic flow rates and loadings to the channelized systems were 17 m^3 d^{-1} (0.2 L sec^{-1}) and 128 m^3 ha^{-1} d^{-1}, respectively, for most of the study period. Hydraulic loadings were increased (2-3 times initial levels) during the first year (beginning in winter) to prevent freezing. As the higher loadings resulted in reduced treatment efficiencies, in the following winter culvert aerators and effluent chamber heaters were installed instead to prevent flow blockage from ice formation. Average influent BOD-5 concentrations and annual loadings (following the first year) were 20 mg L^{-1} (range 3-69 mg L^{-1}) and 86 g m^{-2} (range 74-100 g m^{-2}), respectively, in System 3 and 56 mg L^{-1} (range 10-168 mg L^{-1}) and 294 g m^{-2} (range 239-359 g m^{-2}), respectively, in System 4.

Theoretical retention times were altered by evapotranspiration, ice formation and precipitation. High rates of evapotranspiration in summer tended to increase the retention time causing stagnation and anoxia. In order to increase the rate of flow through the marshes in summer, the water depth was lowered to 5-20 cm. The presence of a 5 cm lip on the outflow chambers prevented the complete drainage of the marshes in summer and, therefore, precluded intermittent drying of the sediment, which would likely have increased the oxygen content of the sediment and contributed to greater contaminant removal in summer (Brinson, 1985). To maintain a water depth of 20 cm and counteract short-circuiting due to ice blockages, water levels were raised to ≥30 cm prior to the onset of winter. Heavy rains may have temporarily reduced the retention time but the resulting dilution tends to balance losses in treatment efficiency. Treatment efficiencies declined when retention time in the marshes deviated from the range of 7-14 days.

Monthly average temperatures of marsh effluents ranged between 0° and 19.6°C (daily temperatures as high as 26.5°C were measured in summer). In December through March, monthly average temperatures were consistently less than 2°C. Monthly average marsh effluent pH values generally fell within the range of 6.5-7.5 (measurements ranged between 6.3 and 8.9).

Routine chemical parameters and fecal indicator bacteria were monitored weekly from April to November and biweekly from December to March. Tests for hydrogen sulphide, phenols and bacterial pathogens were conducted predominantly in winter. Analytical techniques are described elsewhere (MOE, 1981).

Results and Discussion

1. Dissolved Oxygen Levels and Sediment Redox Potential

The Listowel marsh systems demonstrated peak dissolved oxygen levels in spring and fall and varying degrees of oxygen depletion in the summer and winter (Figure 2). The lowest levels occurred in summer when oxygen concentrations in the marsh effluents were generally at or near zero for one or more months. There was a progressive decline in oxygen in the marsh systems during the winter period of ice cover (usually lasting from December through March). The winter decline was often followed by oxygen peaks resulting from spring algal blooms.

The pattern of changes in sediment redox potential at a depth of 1.5-2 cm reflected the variations in dissolved oxygen in the wastewater. Most measurements were between -100 and +240 mV, the zone of facultative anaerobic respiration. A decline in redox potential close to or below -100 mV (the range in which true anaerobes, e.g. sulphate-reducing bacteria, predominate) was measured in summer whereas decreases in redox potential in winter were not as severe. Reductions in treatment efficiency (based on mass balances of wastewater constituents) were observed during the steep decline in redox potential (around -300 mV) in the summer of 1983 when the unusually high evapotranspiration rates caused the formation of stagnant pools of anoxic wastewater.

Both types of pre-treatment had shortcomings with respect to the maintenance of aerobic metabolism in the marshes. The lagoon effluent was usually anoxic in winter due to the ice cover barrier to oxygen transfer and, due to the deep placement of the outflow pump, was uncharacteristically low for lagoons in summer when extensive algae growth is common. The aeration cell did not have sufficient capacity to sustain adequate oxygen levels in the wastewater, particularly during the summer months, and the high solids levels increased the oxygen demand in the marsh. The growth of duckweed on the marsh water surface in summer and the ice cover in winter impeded diffusion of atmospheric oxygen into the marshes.

2. Suspended Solids

Monthly average suspended solids concentrations in the marsh system effluents were generally below 15 mg L^{-1} from fall through spring (Figure 3), often 5 mg L^{-1} or less for extended periods. Elevated concentrations of suspended solids occurred in one or more years in all systems in summer or late spring as a result of algae growth. This was compounded in summer by the concentration of suspended material resulting from evapotranspiration. The high suspended solids loadings from the complete-mix aeration cell effluent caused the development of sludge deposits at the influent end of System 4. These disrupted flow, caused die-back of the cattails and contributed to an elevated oxygen demand in the marsh, but did not significantly affect the marsh effluent levels of suspended solids which were comparable in both systems.

3. Five-Day Biological Oxygen Demand

Marsh effluent BOD-5 levels were generally less than 15 mg L^{-1} during the ice-free months, often between 5 and 10 mg L^{-1} (Figure 4). In the period of January through March, the monthly average BOD-5 levels in Systems 3 and 4 rose slightly in some years to maximum monthly average levels of 26 and 23 mg L^{-1}, respectively. Although low winter temperatures result in reduced microbial activity, substantial reductions in BOD-5 were achieved during the winter months. At loadings experienced in the last three years of the study, winter removal efficiencies ranged between 58 and 82% in System 3 and between 92 and 98% in System 4. Increases in BOD-5 levels occurred occasionally in one or more summer months, reaching maximum monthly concentrations of 32 and 34 mg L^{-1} in Systems 3 and 4, respectively. The elevated summer BOD-5 levels were in most cases coincident with increases in suspended solids concentrations.

4. Phosphorus

Marsh effluent levels of total phosphorus were generally below 1 mg L^{-1} and often below 0.5 mg L^{-1} in the period of fall through spring (Figure 5). Elevated total phosphorus levels occurred in summer (usually July) at which time 67-82% of the total phosphorus was in the soluble fraction. Monthly average total phosphorus values in System 3 exceeded 1 mg L^{-1} during the summer of 1981 (May-Oct.) when alum treatment was suspended and in the summer of 1983 during a period of severe oxygen depletion. System 4 showed higher summer peak total phosphorus levels which occurred in all years and were sustained for more than one month. Marsh effluent soluble phosphorus levels were generally <0.4 mg L^{-1} (often <0.2 mg L^{-1} in spring and fall), increasing in summer to maximum monthly average levels of 1.2 mg L^{-1} in System 3 and 2.2 mg L^{-1} in System 4.

The decline in annual soluble phosphorus removal in Systems 3 and 4 with increases in the cumulative soluble phosphorus loadings is illustrated in Figure 6. Similar results have been reported in several different types of wetlands used for wastewater treatment (Richardson, 1985). The decline in soluble phosphorus removal efficiency over the four years indicates a reduction in the phosphorus adsorption capacity of the sediment and suggests phosphorus saturation of the sediment. Soluble phosphorus in marshes is reported to be immobilized by adsorption and precipitation reactions with aluminum, iron, calcium and clay minerals (Nichols, 1983). The mineral and clay content of the sediment in the Listowel marsh systems was relatively stable due to, the absence of stormwater drainage in the marsh influent and, therefore, the creation of few, if any, new inorganic adsorption sites. Factors contributing to the decline in phosphorus retention were the extended periods of oxygen depletion and the high organic and phosphorus loadings in System 4. Reports indicate that a major mechanism of phosphorus retention in sediments is adsorption onto oxyhydroxides of iron and aluminum (Hook et al, 1973; Day, Jr and Kemp, 1985).

Although the data indicate an annual net export of soluble phosphorus by the end of the study, when summer marsh effluent oxygen levels remained above 2 mg L^{-1} (which occurred in System 3 in 1984 only), 84% soluble phosphorus removal was achieved and soluble phosphorus levels remained ≤0.07 mg L^{-1} in all months. Total phosphorus levels in System 3 effluent during the same summer remained ≤0.2 mg L^{-1}. It may be possible, therefore, that with chemical phosphorus reduction and the maintenance of sufficient dissolved oxygen in the wastewater (to prevent mobilization from the sediment), effluent phosphorus levels can be sustained at low enough levels to meet discharge criteria over the long term.

5. Nitrogen

Marsh effluent total Kjeldahl nitrogen (TKN) concentrations were lowest in the spring and fall (≤10 mg L^{-1}, often ≤5mg L^{-1}). Increases occurred in winter (≤15 mg L^{-1} in System 3 and ≤17 mg L^{-1} in System 4) and summer (≤13 mg L^{-1} in System 3 and ≤23 mg L^{-1} in System 4). On average during the four years, ammonia comprised 63% and 70% of the TKN in the effluent of System 3 and 4, respectively, and showed a similar pattern of variation in the marsh effluents (Figure 7). Monthly effluent ammonia levels declined to ≤1.0 mg L^{-1} for varying lengths of time in the spring and early summer in System 3, whereas ammonia levels in the effluent of System 4 decreased to ≤3.0 mg L^{-1} during this period.

Elevated ammonia levels were observed in the summer and winter in all marsh systems. Ammonia treatment efficiencies were lowest in winter; the decline in ammonia removal began in December or January and lasted through March. Maximum monthly average concentrations were 13 mg L^{-1} and 16 mg L^{-1} in the effluent of Systems 3 and 4, respectively. System 4 showed little ammonia removal during influent peaks in summer and winter with effluent levels often exceeding influent levels. The data suggest that nitrification was inhibited in summer by an inadequate oxygen supply whereas in winter low water temperatures appear to have been the major limiting factor, although low oxygen levels may have also contributed to reduced nitrification. Ammonia in treated effluents could pose a danger to aquatic life in a continuous release system if the receiver does not provide adequate dilution to reduce the oxygen demand imposed by elevated ammonia levels and to maintain un-ionized ammonia below toxic levels. The Ministry surface water objective for un-ionized ammonia is 0.02 mg L^{-1}. Based on maximum levels in the marsh effluents, dilutions of 10:1 would be required to meet this criterion in a receiver with an elevated pH (i.e.pH=8).

6. Hydrogen Sulphide

Hydrogen sulphide levels in the marsh increased at the end of the winter and in summer when oxygen and nitrates were unavailable to satisfy the requirements of heterotrophic bacterial metabolism. Marsh effluent hydrogen sulphide levels remained low (<0.5 mg L^{-1}) through the winter and early spring or in some years (even though lagoon-treated influent contained elevated levels) or remained low until February or March at which times concentrations rose to a maximum of 6 mg L^{-1} in Systems 3 and 4. The elevated hydrogen sulphide levels in the lagoon effluent during the period of ice cover (maximum 12.1 mg L^{-1}) in almost all cases showed improvement after treatment in marsh System 3. Hydrogen sulphide production in summer was observed in all marsh systems in months when sampling was conducted. In Systems 3 and 4, monthly summer levels rose to a maximum of 7.1 mg L^{-1} and 14.5 mg L^{-1}, respectively, whereas the nonchannelized systems exceeded these levels. The dilutions required to consistently meet Ministry objectives of 0.002 mg L^{-1} un-ionized hydrogen sulphide for the protection of aquatic life in surface waters could rarely be met in any of the experimental marsh systems.

7. Phenols

Phenol concentrations in the marsh effluent ranged between (1 and 24 µg L^{-1} and followed a pattern similar to that of hydrogen sulphide as both reflected fluctuations in the availability of dissolved oxygen. The marsh systems receiving lagoon effluent (which contained a maximum phenol content of 21.5 µg L^{-1}) reduced phenols to low levels ((1.5 µg L^{-1}) in the first winter when oxygen concentrations were high. In other years large phenol reductions were observed in System 3 until the end of winter when levels rose (maximum 18.5 µg L^{-1}) in response to the increasing oxygen deficits under the ice. Similar trends were observed in System 4 effluent (maximum 12.5 µg L^{-1}) although influent levels were low. In summer, phenol levels in the marsh effluents often rose above influent levels (maximum 14.0 µg L^{-1} in System 3 and 23.5 µg L^{-1} in System 4). Based on monthly average levels of phenols in the effluent of Systems 3 and 4, dilutions in the range of 14:1 would be required to regularly meet Ministry surface water guidelines of 1 µg L^{-1}, a level set to avoid tainting of edible fish flesh.

8. Fecal Bacteria and Pathogens

Fecal bacteria reductions were high during most of the year with marsh effluent fecal coliform (FC) levels less than or equal to those of Ministry design objectives for disinfected secondary effluent (200/100 ml). However, elevated monthly geometric mean levels (maximum 8,000/100 ml in System 3) occurred in summer and/or winter (Table 1). The detection of maximum levels of FC in the winter months may result from longer bacterial survival at low temperatures (Berg, 1971) and the possibility of short-circuiting due to density stratification and ice blockages. The increases in FC levels in the summer months may be explained in part by the concentrating effect of evapotranspiration. However, the increased numbers of fecal bacteria in summer and winter coincided with the decline in sediment redox potential, and it has been suggested that these conditions give a competitive advantage to the fecal indicator bacteria which are facultative anaerobes (Palmateer et al, 1985). FC levels in the effluent of Systems 3 and 4 were similar although the influent levels in System 3 were 0.1-2.0 % of the levels in the influent of System 4.

Fecal streptococcus (FS) levels showed similar reductions and seasonal trends but the maximum monthly level was higher (maximum 17,000/100 ml in System 3) and generally peaked in July or September. FS has been shown to survive longer than FC at high temperatures (Berg, 1971). Substantial reductions in levels of bacterial pathogens were observed in the marsh system effluents (Table 2). The pathogens were generally detected in the effluent at low levels except for increases in some winter months. Increases in pathogenic bacteria in the effluent were associated with elevated FC levels.

Conclusions

The marsh systems were capable of producing effluent of secondary to tertiary quality. Four year average annual concentrations of the major wastewater contaminants in the influent and effluent of the channelized marshes and average annual treatment efficiencies are listed in Table 3. Large BOD reductions were measured throughout the year despite the low temperature of the wastewater (≤2°C) in the winter months. Removal efficiencies for soluble phosphorus and ammonia were appreciably lower in System 4 indicating the importance of pre-treatment method on marsh system performance.

The oxygen budget proved to be a major influence on the efficiency of wastewater renovation in the marsh systems. Although operating procedures permitted the regulation of marsh hydrology in the attempt to achieve optimal contaminant removal, reductions in treatment efficiency occurred in summer and/or winter during periods of low dissolved oxygen. Elevated levels of ammonia, hydrogen sulphide, phenols and phosphorus in the marsh effluent were generally associated with anaerobic conditions in the marshes. However, low water temperatures were probably responsible for much of the reduction in ammonia removal during winter months when oxygen levels were maintained above 2 mg L^{-1} and should have been adequate to support nitrification.

The data from the experimental systems suggested a number of improvements on marsh design and operation which have been incorporated into a full-scale marshland sewage treatment facility at Port Perry, Ontario. The major modification is the installation at Port Perry of the recommended pre-treatment unit which feeds wastewater to the marshes with a combination of consistently high oxygen levels and low concentrations of suspended solids, hydrogen sulphide, phenols and fecal bacteria. The pre-treatment unit is a 3.1-3.7 m deep partial-mix facultative aeration cell, with an average detention time of 30 days (to provide sludge storage capacity for 20 years) and chemical phosphorus reduction to about 1.0 mg L^{-1} total phosphorus.

The application of marshland wastewater treatment in Ontario depends on contaminant removal at a level which will produce an effluent quality suitable for year-round continuous discharge. A high effluent quality is particularly important in summer during periods of reduced flow and correspondingly low assimilative capacity in receiving waters. Although the problem of reducing ammonia concentrations to tertiary treatment levels (<3 mg L^{-1}) may be more intractable in winter, limitations on marsh application will arise primarily from the sensitivity of receivers during the summer months. The effluent quality produced at Port Perry will provide a better indication of the potential for the application of this type of marshland sewage treatment in Ontario.

References

Berg, G. 1971. Viruses and water quality occurrence and control. Proc. of the 13th Water Quality Conference, Univ. of Illinois, Urbana, Ill.

Black, S.A. 1983. The use of marshlands in wastewater treatment. Proc. Technology Transfer Conference No. 4, Ministry of Environment, Toronto, Ontario, pp. 168-183.

Brinson, M.M. 1985. Management potential for nutrient removal in forested wetlands. In: Ecological Considerations in Wetlands Treatment of Municipal Wastewaters. Godfrey, P.J., E.R. Kaynor, S. Pelczarski and J. Benforado (eds.) Van Nostrand Reinhold Co., N.Y., pp.405-414.

Day, Jr., J.W. and G.P. Kemp. 1985. Long-term impacts of agricultural runoff in a Louisiana swamp forest. In: Ecological Considerations in Wetlands Treatment of Municipal Wastewaters. Godfrey, P.J., E.R. Kaynor, S. Pelczarski and J. Benforado (eds.) Van Nostrand Reinhold Co., N.Y., pp.317-326.

Herskowitz, J. 1986. Listowel Artificial Marsh Project Report. Ontario Ministry of Environment. Water Resources Branch. 253 pp.

Hook, J.E., L.T. Kardos and W.E. Sopper. 1973. Effects of land disposal of wastewaters on soil phosphorus relations. In: Recycling Treated Municipal Wastewater and Sludge Through Forest and Cropland. Sopper, W.E. and L.T. Kardos (eds.), Penn. State Univ. Press, University Park, pp.200-219.

Nichols, D.S. 1983. Capacity of natural wetlands to remove nutrients from wastewater. JWPCF 55(5):495-505.

Ontario Ministry of Environment. 1981. Outlines of Analytical Methods. Laboratory Services Branch. 246 pp.

Ontario Ministry of Environment. 1984. Water Management: Goals, Policies, Objectives and Implementation Procedures of the Ministry of Environment. Water Resources Branch. 70 pp.

Palmateer, G., W.L. Kutas, M.J. Walsh and J.E. Koellner. 1985. Recovery of pathogenic and indicator bacteria from wastewater following artificial wetland treatment of domestic sewage in Ontario. In: Abstracts of the Ann. Meeting of the American Society for Microbiology, Las Vegas, 1985.

Reed, S., R. Bastian, S. Black and R. Kettry. 1985. Wetlands for wastewater treatment in cold climates. In: Future of Water Reuse, Proc. of Water Reuse Symp.III, vol.2, Aug. 26-31, 1984, San Diego, AWWA Research Foundation, Denver, pp.962-972.

Richardson, C.J. 1985. Mechanisms controlling phosphorus retention capacity in freshwater wetlands. Science 228: 1424-1427.

Wile, I., G. Miller and S. Black. 1985. Design and use of artificial wetlands. In: Ecological Considerations in Wetlands Treatment of Municipal Wastewaters. Godfrey, P.J., E.R. Kaynor, S. Pelczarski and J. Benforado (eds.) Van Nostrand Reinhold Co., N.Y., pp.26-37.

Wile, I., G. Palmateer and G. Miller. 1981. Use of artificial wetlands for wastewater treatment. In: Proc. of the Midwest Conference on Wetland Values and Management. Richardson, B. (ed.), June 1981, St. Paul, Minn., pp.255-271.

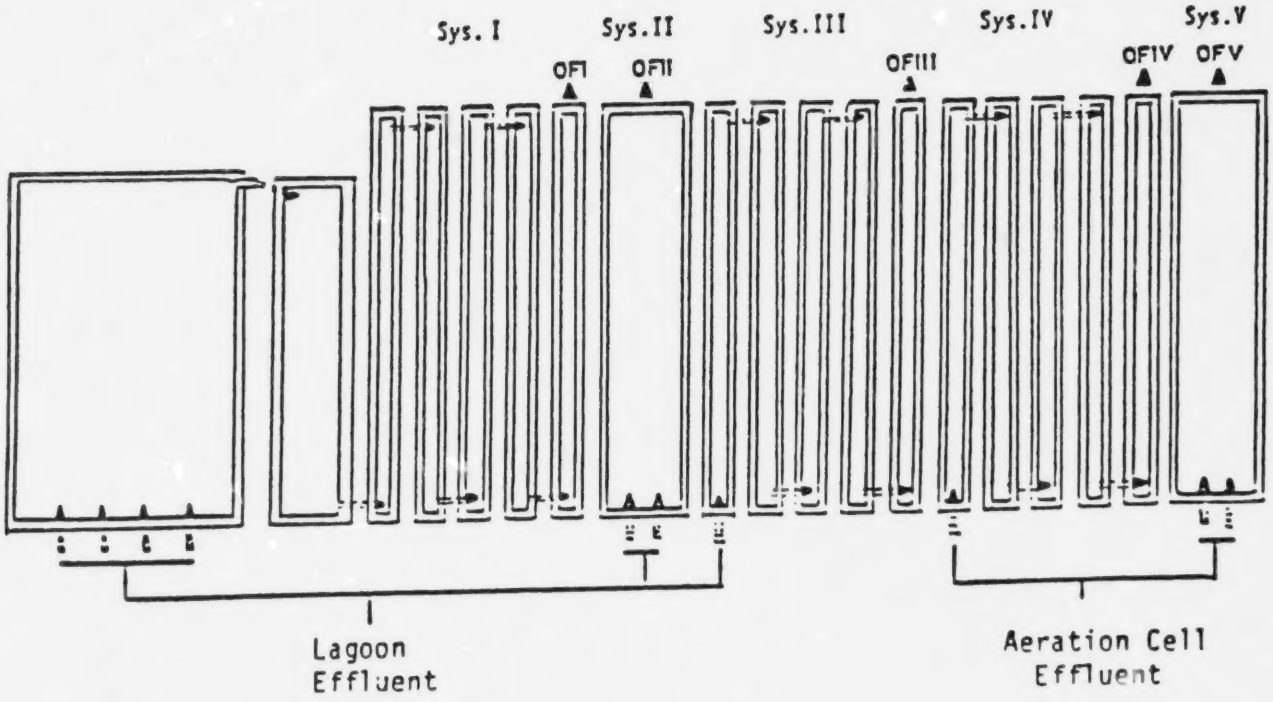
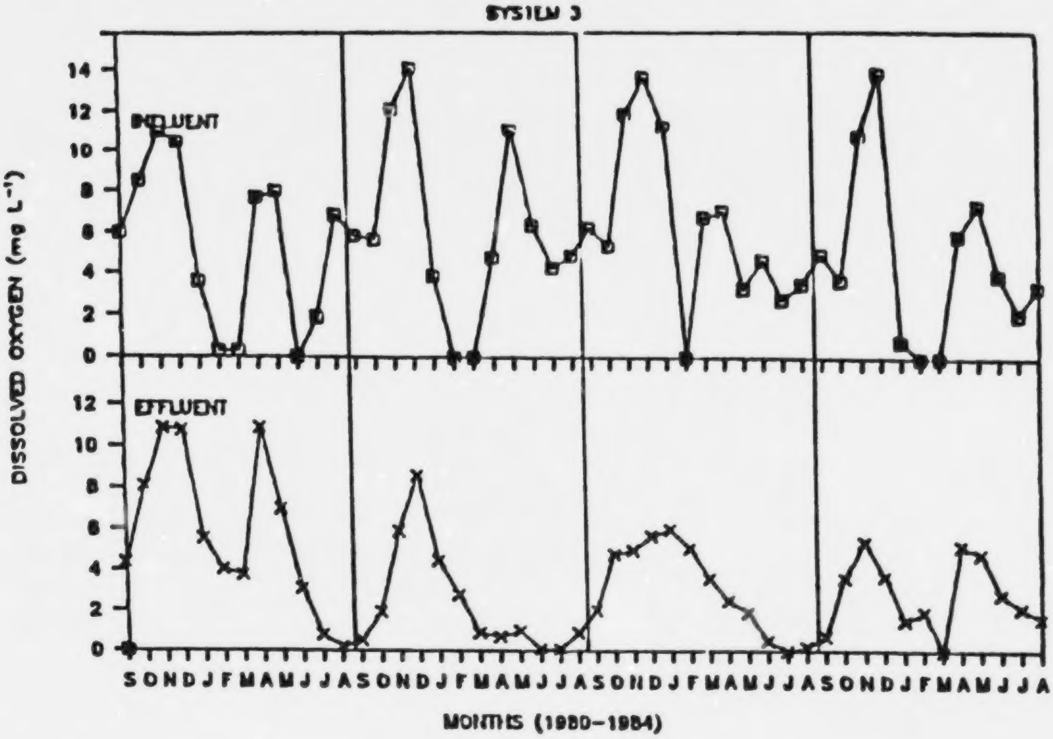


Figure 1. Design of Listowel marsh systems.



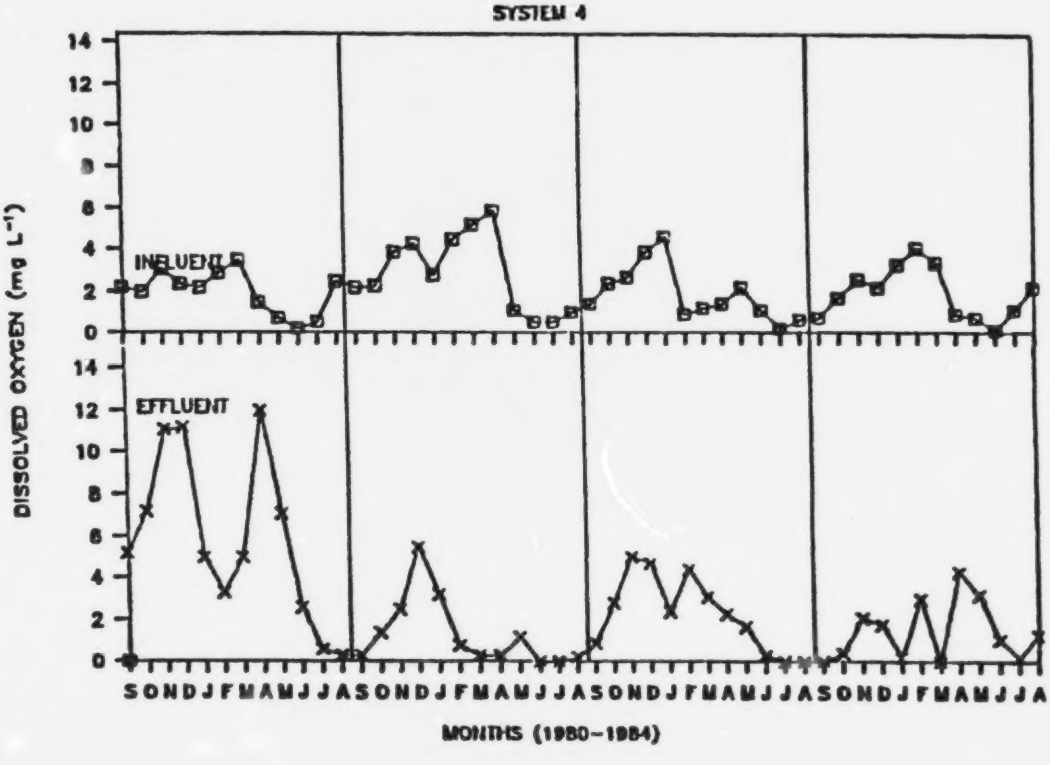
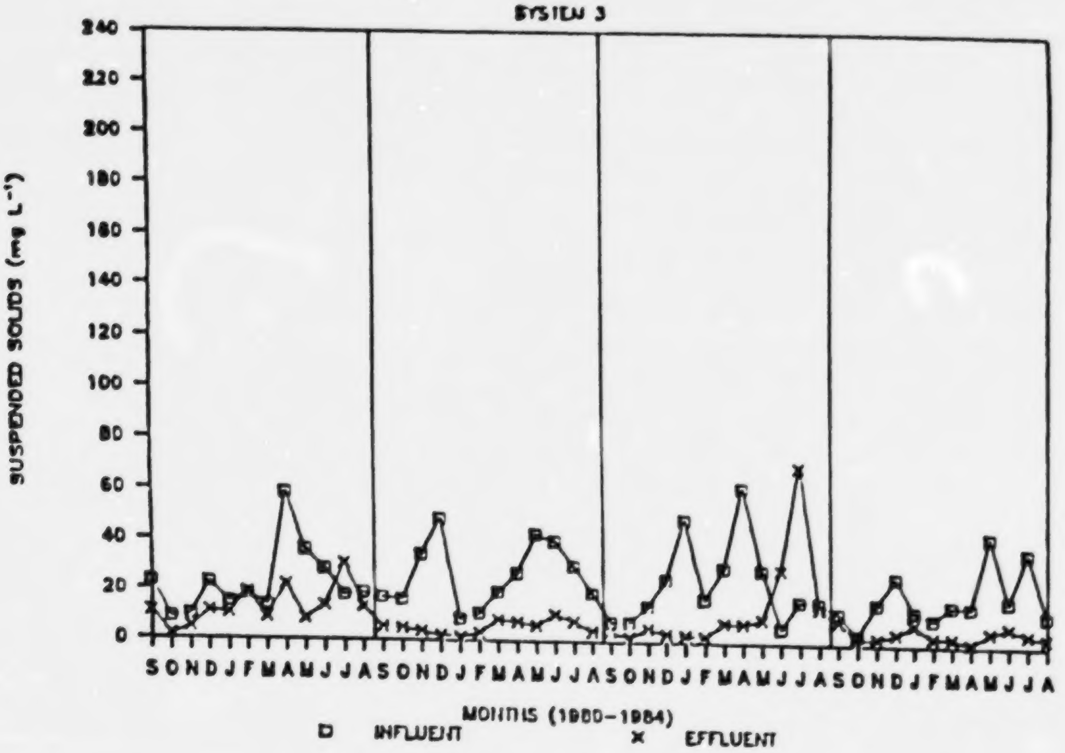


Figure 2. Monthly average dissolved oxygen levels in System 3 (treating lagoon effluent) and System 4 (treating aeration cell effluent).



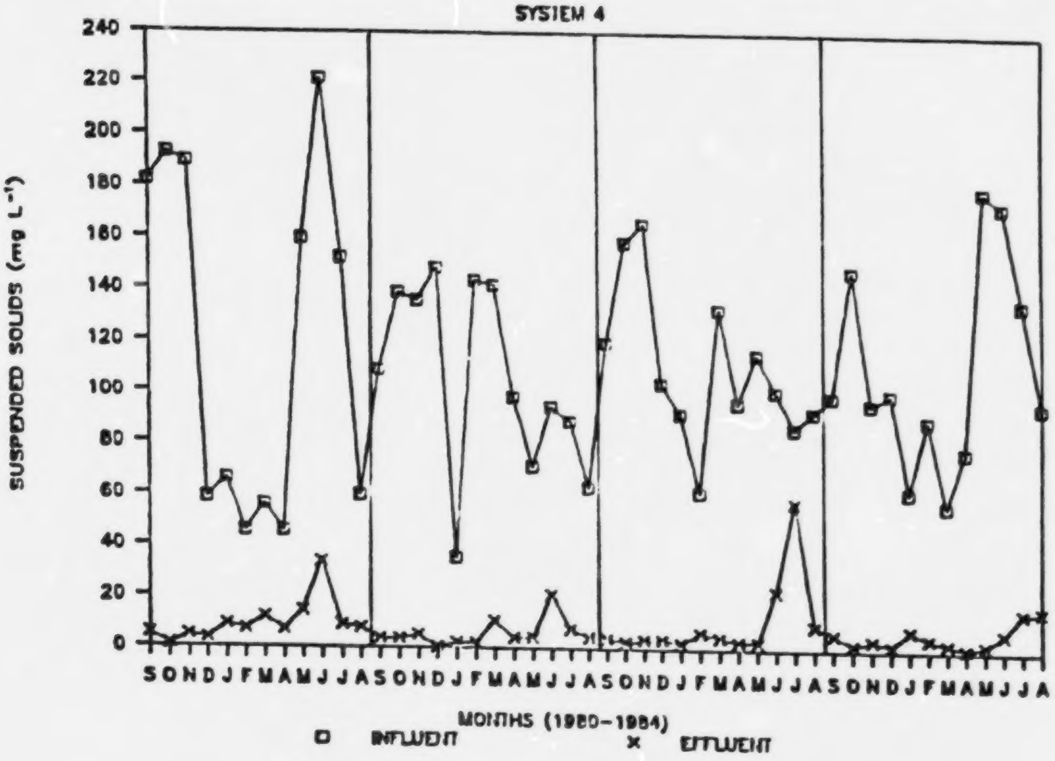


Figure 3. Monthly average suspended solids levels in the influent and effluent of Systems 3 and 4.

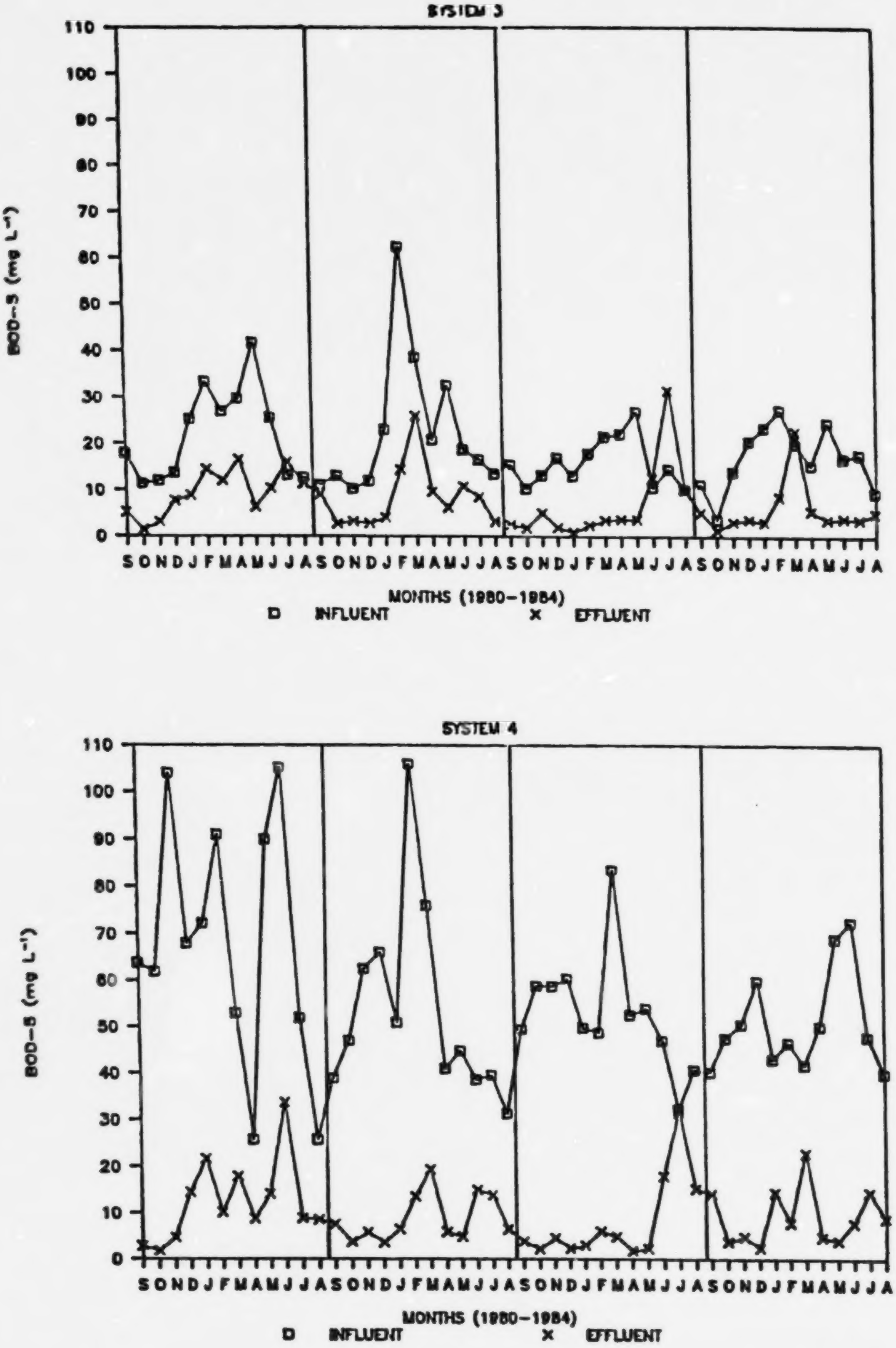
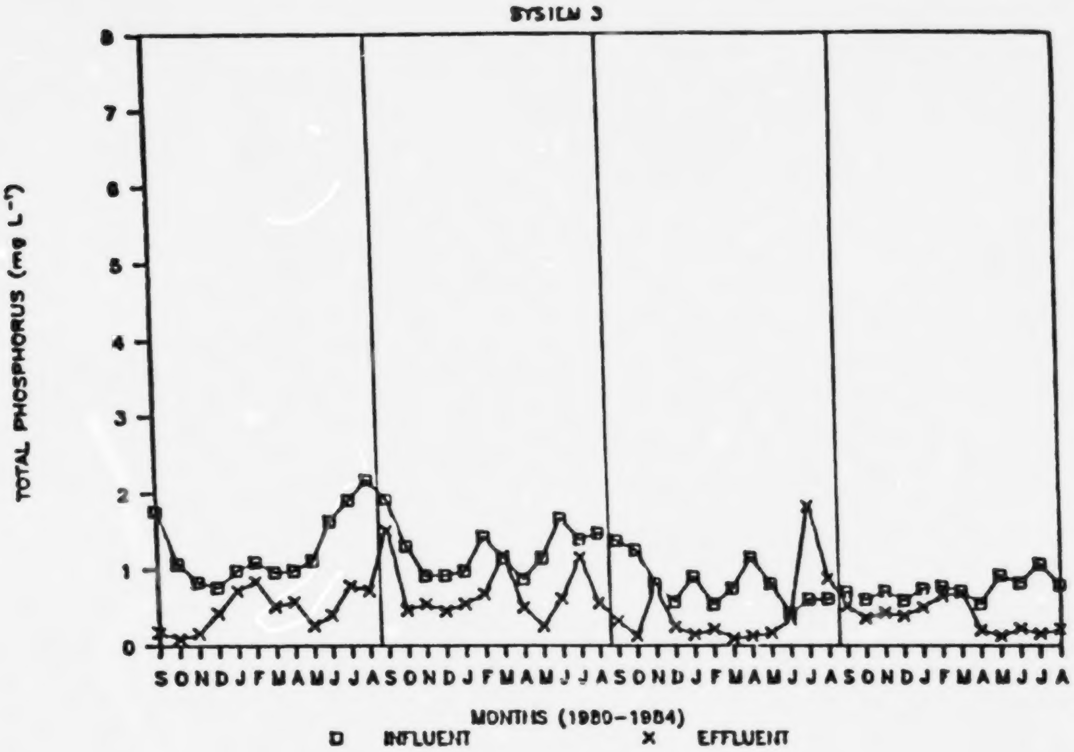


Figure 4. Monthly average BOD-5 levels in the influent and effluent of Systems 3 and 4.



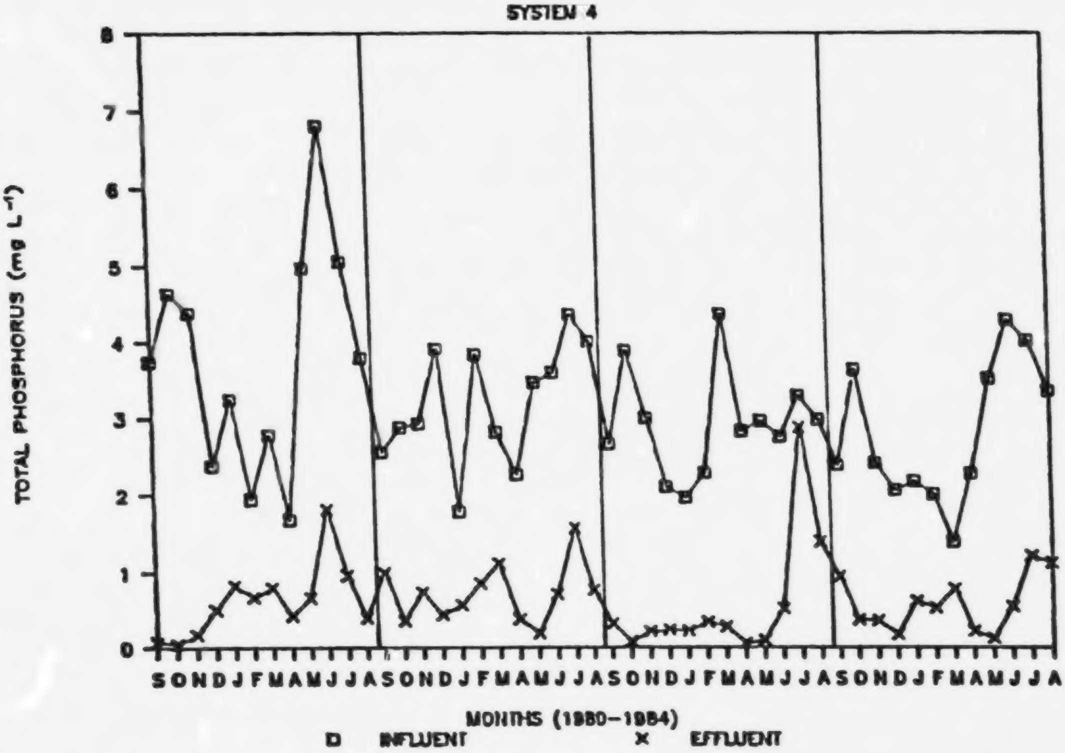


Figure 5. Monthly average total phosphorus levels in the influent and effluent of Systems 3 and 4.

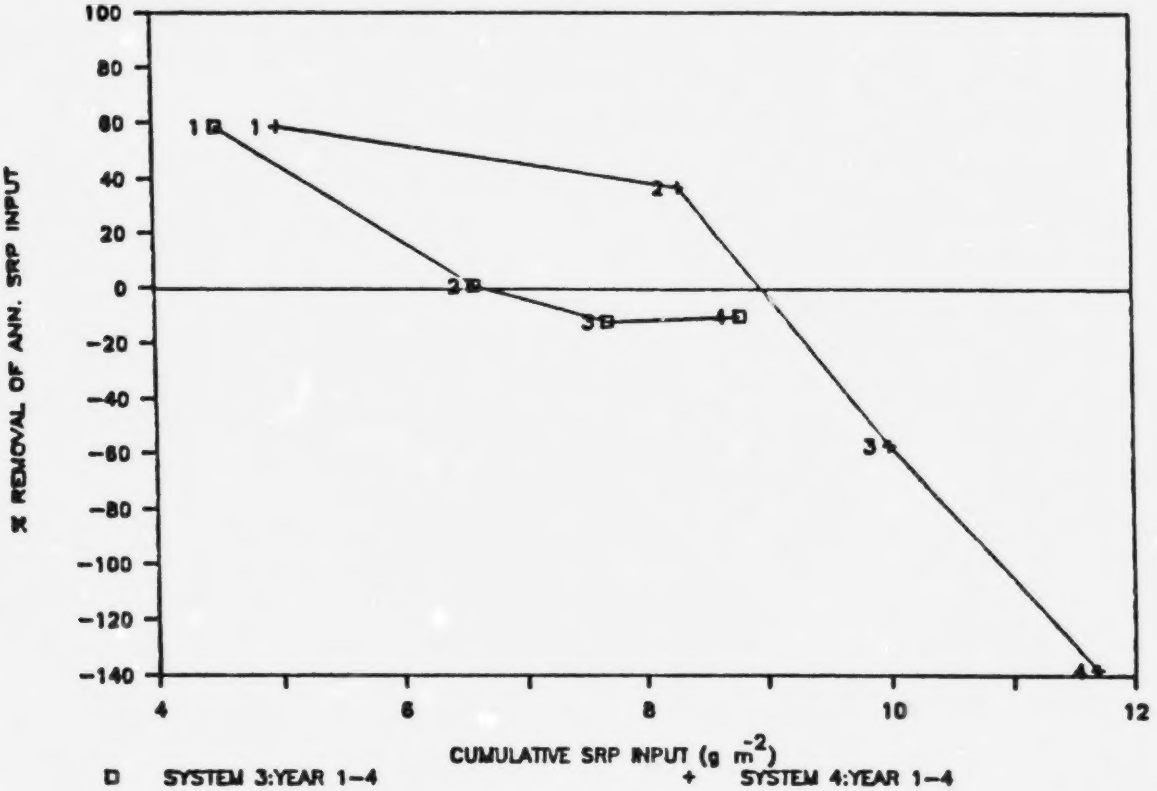


Figure 6. Cumulative soluble reactive phosphorus (SRP) loadings and annual removal rates in Systems 3 and 4.

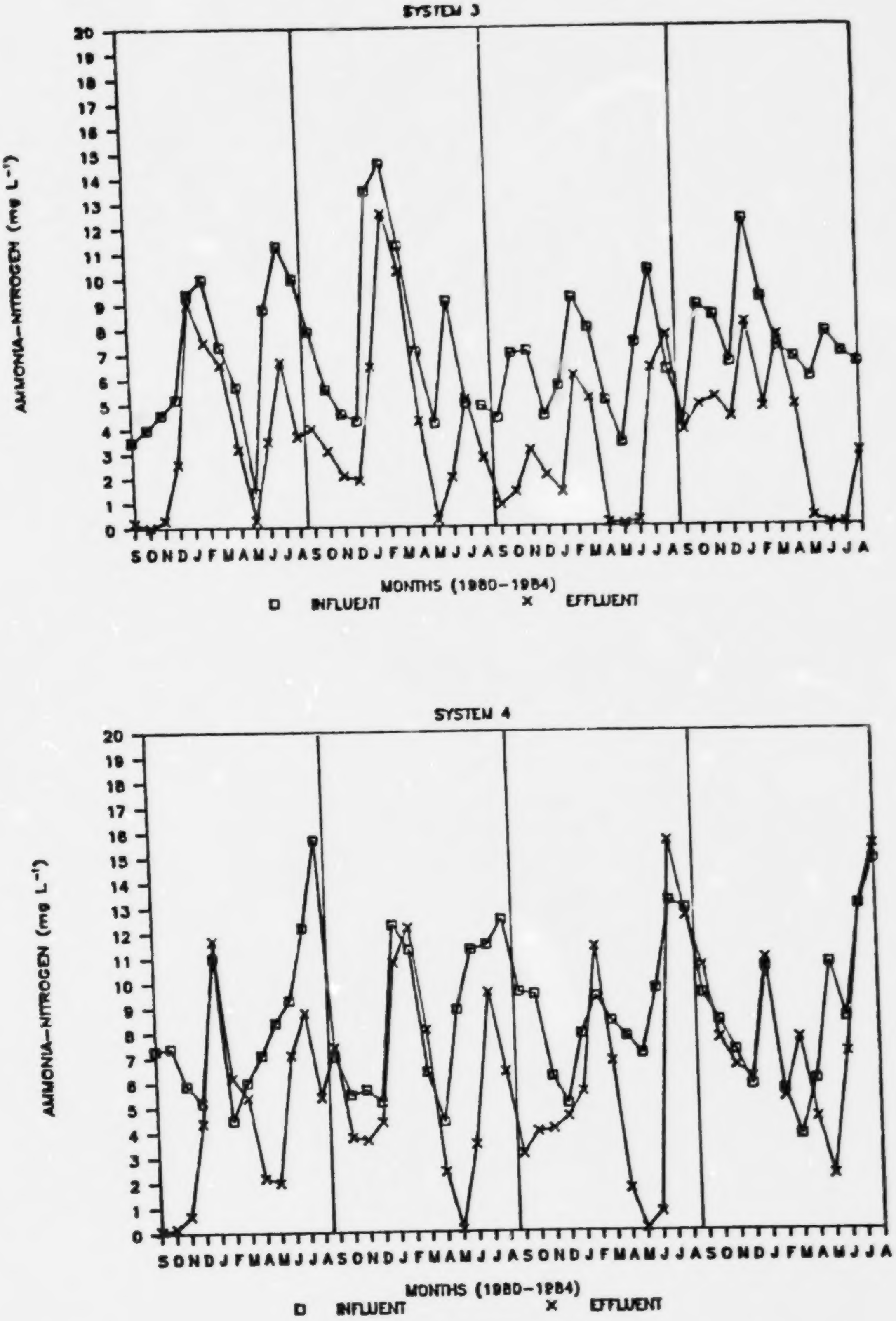


Figure 7. Monthly average ammonia-nitrogen levels in the influent and effluent of Systems 3 and 4.

Table 1. Monthly Average Geometric Mean Levels of Fecal Coliform Bacteria Over Three Years (1981-1984)

	System 3			System 4		
Month	Influent	Effluent	% Reduction	Influent	Effluent	% Reduction
Sept.	205	44	79	216,125	467	> 99
Oct.	573	21	96	314,647	248	> 99
Nov.	4,343	18	> 99	293,662	373	> 99
Dec.	3,095	36	99	421,269	57	> 99
Jan.	46,154	15	> 99	386,224	603	> 99
Feb.	80,678	223	> 99	382,320	1,017	> 99
Mar.	36,726	3,058	92	164,204	2,043	99
Apr.	3,544	109	97	169,275	34	> 99
May	626	37	94	172,472	27	> 99
June	288	641	-123	183,873	334	> 99
July	376	697	-85	182,240	1,353	99
Aug.	206	304	-48	153,736	297	> 99

Bacterial levels in numbers per 100 ml.

Table 2. Geometric Mean Levels of Fecal Coliform Bacteria (FC), *Yersinia entercolitica* (YE), *Clostridium perfringens* (CP), *Pseudomonas aeruginosa* (PA) and *Salmonella* spp. (SSP) in the Channelized Marshes Over Three Years (1981-84).

	FC		YE		CP		PA		SSP	
	Inf	Eff	Inf	Eff	Inf	Eff	Inf	Eff	Inf	Eff
System 3										
Geometric Mean	1,736	53	4,241	300	1,036	6	10	1	-	-
Frequency of Occurrence	100%	100%	63%	63%	88%	48%	100%	100%	67%	8%
System 4										
Geometric Mean	222,990	121	28,602	563	13,148	4	662	2	-	-
Frequency of Occurrence	100%	100%	69%	75%	96%	39%	100%	100%	83%	25%

Influent (Inf) and effluent (Eff) bacterial levels are in numbers per 100 ml. FC and PA tests conducted weekly (bi-weekly in winter); YE and CP tested predominently in winter. SSP analyzed for presence or absence; samples (N=12) tested in alternate months in 1981 and 1982.

Table 3. Average Wastewater Concentrations and Treatment Efficiencies in Systems 3 and 4 (1980-1984)

System 3: Channelized marsh receiving lagoon effluent

	Average Conc. (mg L^{-1})		% Removal Based on Mass Balance				
			Years				
Parameters	Influent	Effluent	1	2	3	4	Avg.
Suspended Solids	22.8	9.2	40	75	53	73	61
BOD-5	19.6	7.6	57	56	63	62	59
Total Phosphorus	1.0	0.5	53	39	47	45	46
Soluble Phosphorus	0.37	0.26	59	1	-12	-10	9
Total Kjeldahl-N	12.0	6.1	32	41	54	46	43
Ammonia-N	7.2	3.8	31	32	51	42	39
Un-ionized Ammonia-N	0.13	0.01					
Nitrate-Nitrite-N	0.25	0.23					
Hydrogen Sulphide*	1.8	1.0					
Un-ionized H2S*	1.31	0.65					

System 4: Channelized marsh receiving aeration cell effluent

	Average Conc. (mg L^{-1})		% Removal Based on Mass Balance				
			Years				
Parameters	Influent	Effluent	1	2	3	4	Avg.
Suspended Solids	111.1	8.0	90	93	93	94	93
BOD-5	56.3	9.6	78	80	88	81	82
Total Phosphorus	3.2	0.6	79	76	84	78	79
Soluble Phosphorus	0.40	0.34	59	37	-57	-138	-25
Total Kjeldahl-N	18.7	8.7	49	46	55	41	48
Ammonia-N	8.6	6.1	28	22	35	5	23
Un-ionized Ammonia-N	0.07	0.02					
Nitrate-Nitrite-N	0.38	0.21					
Hydrogen Sulphide*	0.20	1.31					
Un-ionized H2S*	0.13	0.81					

---

* The dates and frequency of hydrogen sulphide analyses varied between years; most samples collected in winter.

Tests of a Hydrocyclone Designed for Sewage Treatment

by J.D. Boadway

Report on Project No. 184 PL

Summary

This report deals with pilot plant tests of a hydrocyclone designed for use in sewage treatment.

The unit proved capable of handling 36.4 liters/second of inflow when a differential pressure of 6 meters of water was applied. The reject flow could be varied from 0.5 to 5.0 liters per second by use of differing sizes of reject orifice and differing outlet pressures.

The unit achieved 100% removal of the grit used in tests which included sand particles of 60 microns in diameter and also removed fine sawdust and organic material from vegetable washings.

This hydrocyclone can be operated at low pressures and was designed specifically for use in sewage treatment. This may prove to be a new and useful tool and is now ready for field trials. The decision as to the nature and location of those trials needs now to be decided by the Ministry.

Introduction

The Ministry of Environment informed the author in June of 1985 of a grant, known as Project No. 184 PL, to develop a special design of hydrocyclone, which could be used with low pressure differential, to remove grit from sewage. The original proposal was that a unit would be designed after consultation with the Ministry. This design would then be built and tested at Queen's University. Finally any necessary modifications would be made to the unit and it would be installed in a sewage treatment plant for field testing.

A report (Ref. 1) was written by the author and submitted to the Ministry on August 6, 1985. This report discussed the theory of hydrocyclone design and outlined the design parameters of a hydrocyclone with their probable effects. Following a discussion with Mr. Henry Kronis, the liaison officer with the Ministry, a hydrocyclone deemed most suitable for sewage treatment was designed and a report (Ref. 2) sent to the Ministry to describe the final design and its expected performance. Blueprints of the unit were sent out for quotes from three possible fabricators. The installation for testing the equipment was designed while waiting for their response as reported in the author's spring report (Ref. 3).

The lowest construction bid was from Wejay Machine Products Company of Kingston. However, because the design was much larger in size than that anticipated when submitting the original proposal it was necessary to reduce the scope of the project slightly by having only one of the alternate cone designs built and to use for construction of the hydrocyclone funds which had originally been intended for other aspects of the research. The unit was delivered in late April and work begun upon the test installation. Whereas the completion of the installation was expected by the first of July, diversion of personnel to other work and problems in erecting the equipment delayed completion until the second week in August. Students were employed as research assistants until September 12 and tests conducted to give the results presented in the report that follows.

While employed in the paper industry between 1952 and 1963, the author was involved in research on hydrocyclones, which were marketed under the tradename of "Vorject" and "Vorvac," and has also been studying the present design of hydrocyclone since 1978, and has taught environmental engineering for 20 years. The report will hence include remarks which stem from experience and unpublished information as well as the observations from the brief period of test on the unit and published papers of other investigators. Attempts will be made to avoid excessive repetition of material covered in the previous reports to the ministry.

Hydrocyclones

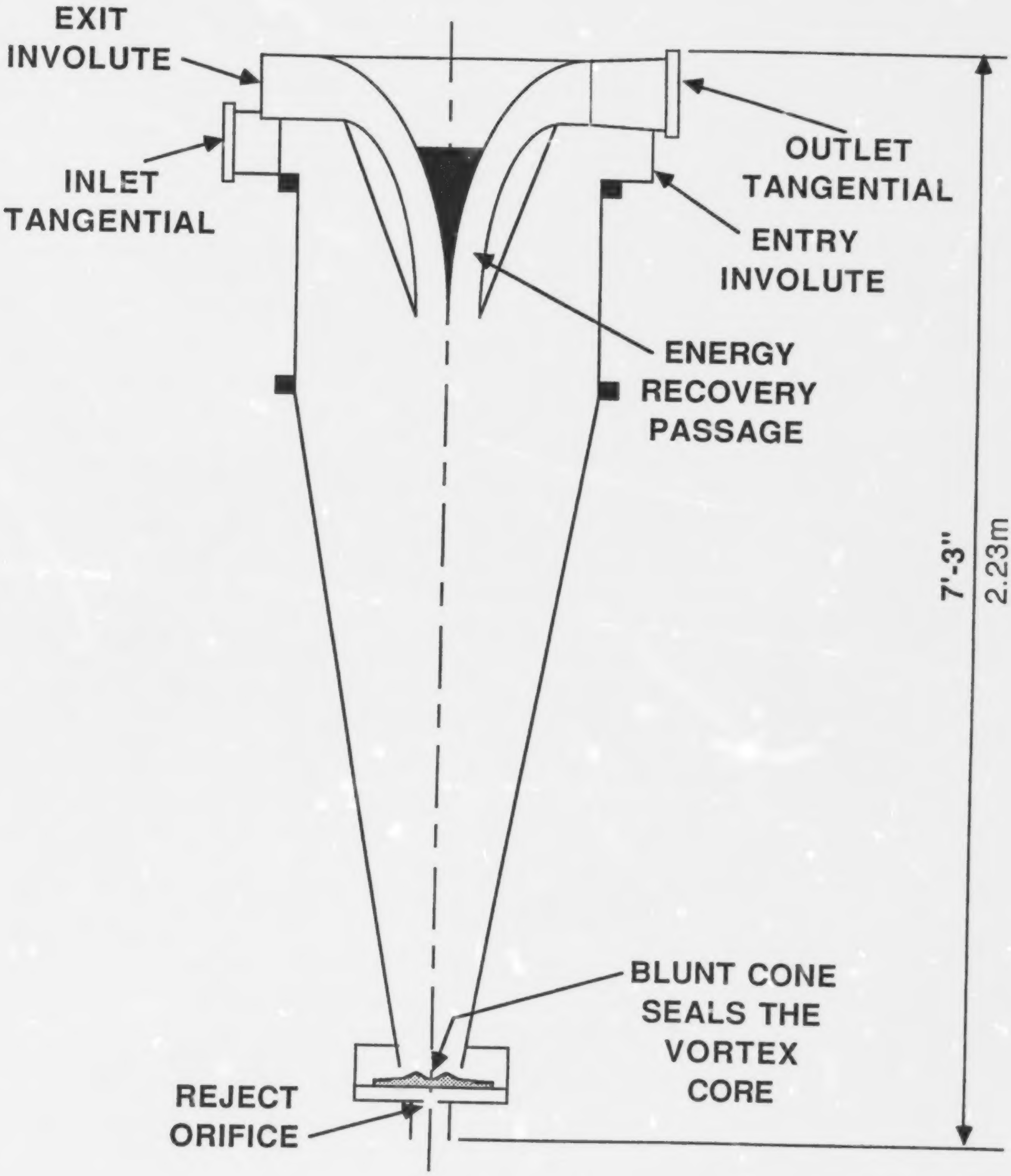
Hydrocyclones could be loosely defined as fluid containers in which a vortex is produced with sufficient resulting centrifugal force to bring about a separation. The text written by Bradley (Ref. 4) defines the broad range of these devices used for different purposes and dwells, for a considerable length, on the more common conical type. The early device of Freeman, sold under the name "Vortrap", was used for some time in sewage treatment (Ref.5). This device, which operated at low pressure drop, was developed in the paper industry for removal of grit and tramp metal.

There also has been use of the conical design known as the "Dorclone" (Ref. 6) for washing of grit. There have been attempts to use existing commercial designs of fluid cyclones but blockages have usually led to operating problems.

In more recent times there has been some use of a device called a "Swirl Chamber" (Ref. 7) in sewage treatment. This device is not a hydrocyclone but merelya circular clarifier of very high overflow rate in which the secondary currents induced in the boundary layer are used in place of mechanical arms to convey the settled solids.

To the author's knowledge there has not been any attempt to design a hydrocyclone specifically for use in sewage treatment. Such a design should operate at lower pressure, be very flexible in operating pressures to accommodate changes in flow and should, if possible, be free from problems of blockage from foreign objects so that it can operate without protection from screens. It should be capable of removal of all mesh sizes of grit and courser organic sediments. The development of a form of hydrocyclone, in which the energy in the exit fluid is converted into pressure, showed excellent promise of meeting that need and led to the submission of the

Figure 1 Energy Recovery Hydrocyclone



proposal to the Ministry and the grant of Project No. 184 PL.

The design which resulted was described in Reference 2 and the final version as manufactured for tests is shown in Figure 1. Fluid enters by an involute inlet, to minimize energy loss by turbulence, into a cylindrical section forming a vortex. The high tangential velocity, which becomes even larger as the fluid spirals inwards to smaller radii, leads to centrifugal forces which cause dense solids to migrate outward to the boundary layer next the wall. This boundary layer carrying the particles moves downward along the wall of the cone, due to the radial pressure gradient, and passes outward around a blunt cone and then spirals inward to discharge through a bottom orifice.

What makes this design special is that the fluid leaving the top passes through a gradually expanding coaxial passage which curves outward to an involute exit. This converts velocity in the vortex to pressure and results in a sucking effect which creates a vacuum at the core of the vortex. The conical barrier at the bottom end prevents air insuction and provides a recess for stabilizing the bottom end of the vacuum core. A net result is that whereas the pressure at the core of most hydrocyclones is atmospheric pressure, there is a vacuum at the core of this design. The larger pressure differential across the vortex leads to a high flow and tangential velocity especially when the inlet pressure and differential pressure are low. Thus the hydrocyclone can operate and separate effectively at lower pressures. In addition, since the reject end has a baffle which prevents air insuction, the unit can operate with both outlet and inlet pressures varied over a broad range.

The unit shown in Figure 1 is the straight cone version indicated as an alternate in the previous design report. It was decided not to build the more expensive curved cone design because of limited funds available. The curved cone is thought to give better separation in oversize solids, less abrasion and a lower reject flow. Also, whereas the original design showed the curved exit surfaces as being made of fibreglass, the fabricator chose to make some parts of expanded aluminum. The unit cost $10,600 of which a portion was for tooling.

Test Installation

The pilot plant installation is shown schematically in Figure 2 and also in the photograph Figure 3.

The tank had been used for previous tests on smaller hydrocyclones but had to be modified to accommodate the larger outflow without leading to a vortex at the outlet. The pump was well under capacity for handling the larger flow and thus limited the pressure which could be applied. The high velocity through the pump may have contributed to turbulence in the inlet fluid and pressure fluctuations.

Figure 2 Installation Schematic

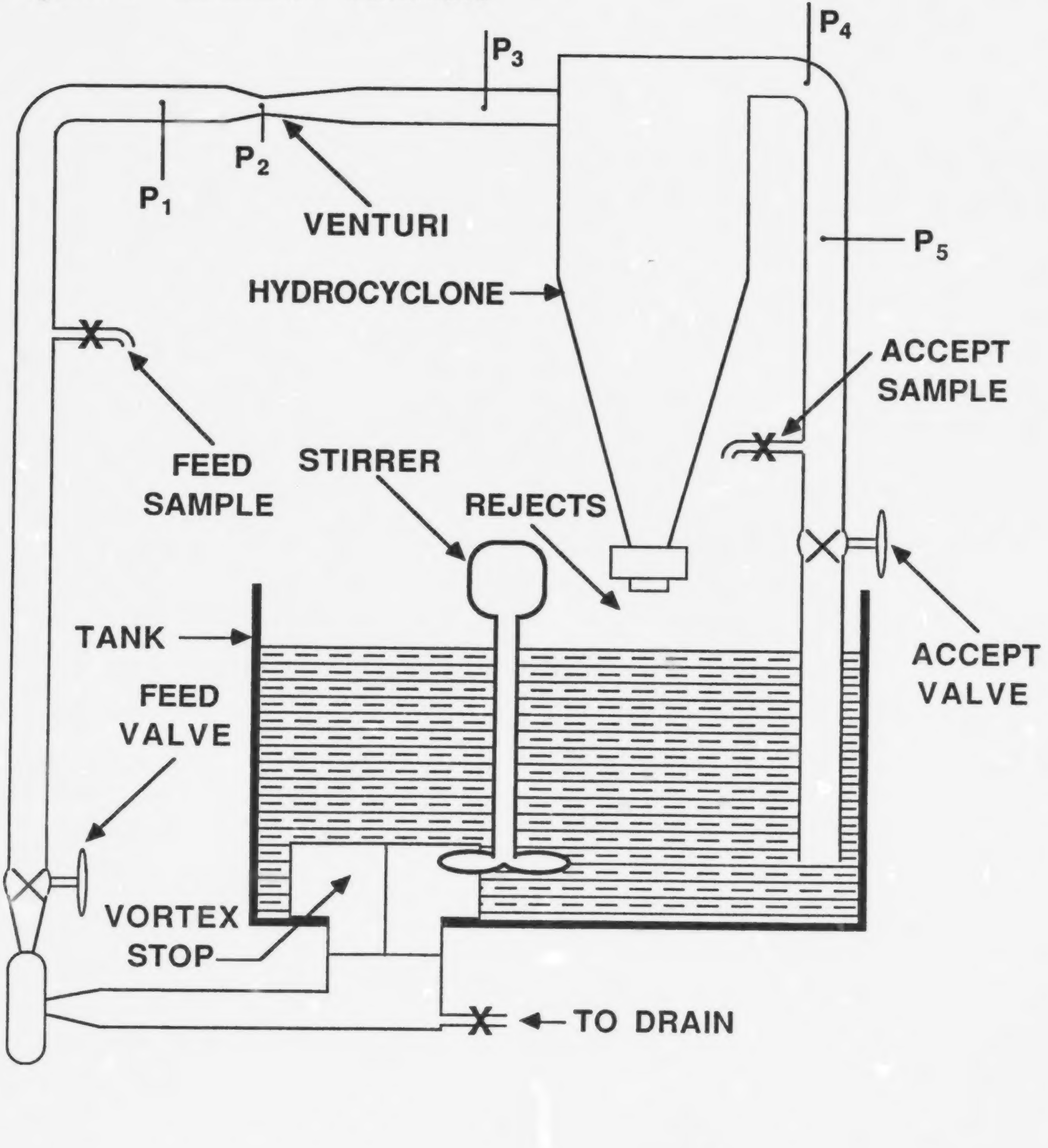


Figure 3 Test Installation

The piping system was of 6" aluminum tubing with standard 25 lb flanges. Gentle tapered reducers were fabricated to connect to the 4 inch inlet and 3 inch outlet of the pump. A Venturi meter was constructed for measuring the inlet flow and calibrated in Queen's hydraulics laboratory. The hydrocyclone was supported by a metal frame and also by a cable connected to an eye bolt through the floor into the office above.

Pressure measurements were taken at 5 locations, namely:

1. Inlet to the Venturi meter
2. Throat of the Venturi meter
3. Inlet to the hydrocyclone
4. On the side of the elbow on the exit
5. On the down pipe for the hydrocyclone

While a sensitive digital pressure meter had been purchased for the project, it was found to be unsuitable due to pressure fluctuations and a mercury manometer was used to measure the pressures during tests.

Hydraulic Tests

1. Scaling

It is essential to have detailed knowledge of the hydrocyclone to design future installations. It is also desirable for the author to have detailed hydraulic knowledge to ensure that the unit is performing according to design and to provide him with the background to design other units.

The unit being tested has a diameter of 25 inches (63.5 cm) and length of 7.4 feet (2.32 meters). It has been scaled up by a factor of 2.5 from a unit which had been tested previously.

The flow should be proportional to the square of the diameter and this relationship was used to produce the predicted inlet flows in the previous report.

2. Inlet Flow

The inlet flow was measured using the Venturi meter. These measurements are shown plotted in Figure 4 against the pressure differential across the hydrocyclone. A statistical analysis of the data was carried out and the inlet flow was found to be related to pressure differential by the equation below.

$$Q_i = 14.38\sqrt{\Delta H + 0.38} \quad \text{-- equation 1}$$

where Q_i = Inlet flow (liters/second)

ΔH = Pressure differential (meters of water)

Figure 4 Inlet Flow

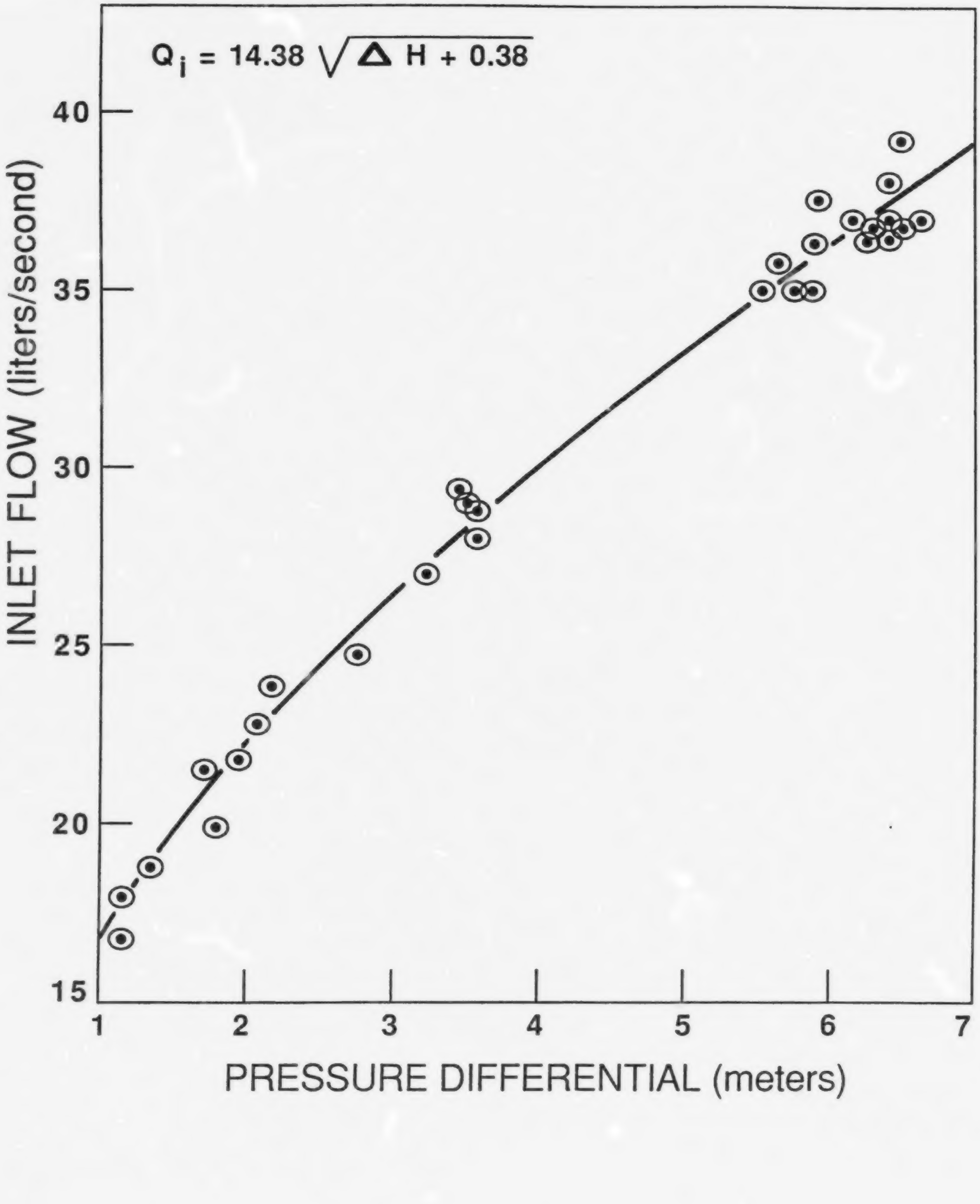
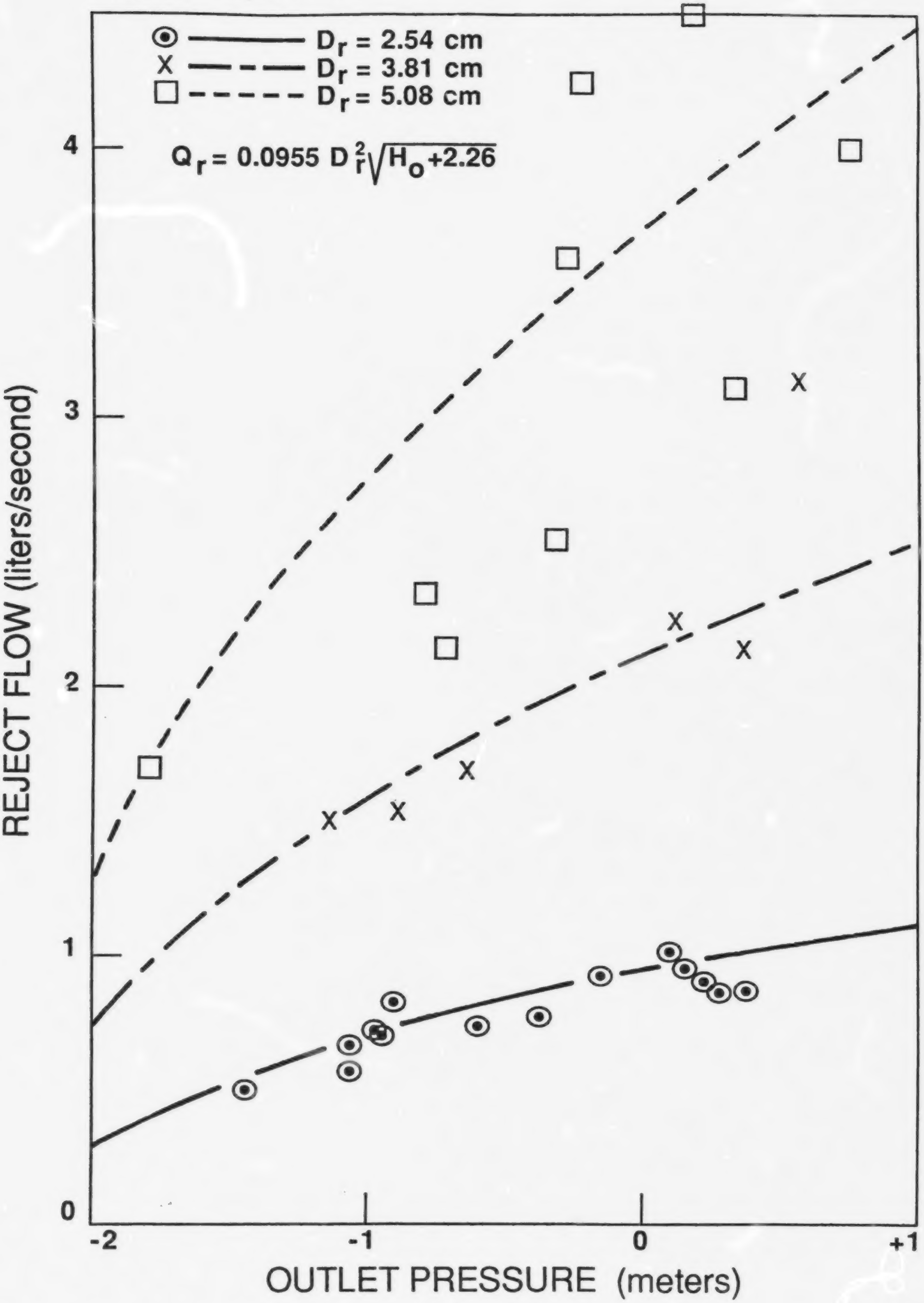


Figure 5 Reject Flow



This equation is shown plotted as the line in Figure 4. The observed flows agree with predicted flows at low pressure but are about 10% low at high pressure differential.

The scatter of observed points about this line is about ± 5 liters/second. An analysis of the effect of other variables such as reject flow, reject orifice size and outlet pressure revealed them as being not significant. The three readings prior to the hydrocyclone oscillated by ± 1/10 meter of water, which also effects flow readings by ± 10 liters/second. Thus variations in flow determinations due to turbulence could well explain the scatters of point about the line. It should be noted that the readings after the hydrocyclone showed very little oscillation. Thus the condition at the pump and turbulence in the pipeline rather than the hydrocyclone lead to the oscillations.

3. Reject Flow

Measurements of reject flow were made by using a stop watch to measure the time to collect 10 $^1/2$ liters in a pail. The resulted data is shown plotted in figure 5 against outlet pressure with different symbols to show the effect of the use of differing reject orifices. Again, as with inlet flow, the data was subject to extensive statistical analysis to develop the following equation.

$Q_r = 0.0955\, D_r^2 \sqrt{H_o + 2.26}$ -- equation 2

where Q_r = Reject flow (liters/second)
D_r = Reject orifice diameter (cms.)
H_o = Outlet pressure (meters of water)

This equation is also shown plotted in figure 5 as three lines corresponding to the three sizes of reject orifice used in tests.

The data fits the curve for the 1" (2.54 cm) and the 1 1/2" (3.81 cm) orifice quite well but scatter widely about the curve for the 2" (5.08 cm) orifice. At these high flows the times to fill the 10 1/2 liters in the pail were between 2 and 5 seconds with possible variation of ± 1 second. Much of this variation was due to observable fluctuation in reject flow which was particularly noticeable with low outlet pressure. An average of 6 readings was taken in attempt to minimize the error in these readings. As will be noted in figure 5 averaging still did not eliminate the scatter about the curve.

Attempts were made to explain these discrepancies by incorporating other variables in the equation. There was a minor tendency for reject flow to be less with higher differential but the effect was not statistically significant.

With normal discharge through an orifice the pressure differential becomes the axial velocity head and the equation for flow becomes

$$Q = Cd\,A\sqrt{2\,gH} \quad \text{-- equation 3}$$

where Q = flow through the orifice
A = cross sectional area of the nozzle
g = gravitational constant
H = the pressure differential
Cd = a dimensionless discharge coefficient of between 0.55 and 1.0

The value of H for the reject orifice is the $(H_o + 2.26)$ in equation 2, the 2.26 being due to the distance of the reject orifice below the outlet. If one expresses equation 2 in consistent units in the form of equation 3 the value of Cd becomes 0.27 which is ridiculously low. The reason for this is that the throttling in this type of "Vortex Nozzle" (Ref. 8) is through the pressure differential across the vortex which approaches the opening due to centrifugal forces. The rejects issue through the orifice as a hollow cone spray with no fluid in the centre.

The throttling effect of a vortex between parallel plates depends upon the tangential velocity of fluid entering, the density of the fluid and the fluid viscosity as well as the geometry of the system. It has been observed that when this type of nozzle is used in controlling the discharge from hydrocyclones that the reject flow will automatically rise when there is a larger content of oversize solids in the feed. This is the most probable reason for fluctuation in reject flow as the mixer in the centre of the tank may not always blend the accepts and rejects perfectly as they proceed to the tank outlet.

The separating efficiency of the hydrocyclone is dependent upon the percentage rejection, as will be discussed later. This requires use of both equation 1 and 2 incorporated into a new equation

$$R = 100\,\frac{Q_r}{Q_i} = 0.664\,D^2\,\sqrt{H_o + 2.26)/(H_i - H_o + 0.38)} \quad \text{-- equation 4}$$

where R = percent solids rejection
H_i = Inlet Pressure (meter of water)
other terms as previously defined

Solids Removal

1. Theory

Particle removal, in sewage treatment methods, is usually by settling in tanks or clarifiers. One design parameter used is the overflow rate, which can be expressed as the settling rate of particles which should just be removable at 100% efficiency.

$$S_o = \frac{6Q}{A} \quad \text{-- equation 5}$$

where S_o = settling rate cms/minute
Q = flow cubic liters/second
A = surface area of the clarifier meters^2

The efficiency of removal of a particle of settling rate S is then given by the equation below.

$$E(S) = \begin{cases} 100 \text{ for } S \geq S_o \\ 100 \times \frac{S}{S_o} \text{ for } S < S_o \end{cases} \quad \text{--equation 6}$$

Turbulence or thermal currents in a clarifier usually prevent the theoretical efficiency from being achieved.

The literature on hydrocyclones expresses removal capability in terms of the diameter of particle removable at 50% efficiency i.e. d_{50} (Ref. 4). The reason for this is that efficiency versus percent removal curves from experiments are very steep at this point. However, the resulting emperical and also some theoretical (Ref. 9) equations also contain density difference between the particles and that of water and can hence be expressed using Stokes Law as equivalent settling rates of the same particles in still water or S_{50}. The design of hydrocyclones is still not an exact science and there are discrepancies in the equations of various authorities and also with the author's past research. One could, however, express all the design equations for scaling of one design in terms of S_{50} by the equation below.

$$S_{50} = k \frac{D^{n1}}{(\Delta H)^{n2} (R)^{n3}} \quad \text{--equation 7}$$

where S_{50} = settling rate of solids removable at 50% efficiency
D = diameter of the hydrocyclone
ΔH = pressure differential
R = % Reject rate
n1 = exponent between 1 and 3
n2 = exponent probably 0.5
n3 = exponent probably 0.32
k = a constant dependent upon design proportions

Whereas most theoretical and experimental investigators would agree on the values of n2 and n3 indicated above, there is little agreement on the value of n1.

Assuming viscous conditions and constant resistance to settling, independent of scale, the n1 = 1. However if settling is impeded by turbulence which is dependent on diameter, the n1 might be expected to have a higher value, the increase depending upon the design. In the previous reports of References 1 and 2 it was assumed that effect of turbulence would be reduced because of the design proportions and an involute rather than tangential inlet, thus n1 was taken as 1.

Although Stokes Law may be used to obtain the settling rate of spherical or granular particles it does not apply very well to particle shapes such as fibers or platelets which have a large surface for their mass. The fluid shear and turbulence in hydrocyclones acts upon high surface particles, such as fibres, and sweeps them out of the boundary layer into the inner stream. The use of hydrocyclones to clean pulp suspensions in the paper industry is based upon this effect.

In the author's previous research he used settling tests while using the hydrocyclone to remove silica flour from water. These tests were time consuming but produced a curve of removal efficiency versus settling rate. Equation 6 fitted the experimental data quite well, however, more complex equations which led to a curvature at the top end as efficiency approached 100% gave a better fit. Unfortunately, because of the delay in the installation of the equipment and difficulty in obtaining research assistants after classes began, it was decided not to use this time consuming technique.

2. Grit Separation

A fine grade of sand was used for grit tests with a mean particle size approximately 100 microns. Samples of 10 1/2 liters volume were taken of feed to and accepted fluid from the hydrocyclone during its operation. These samples were then washed through 100, 200 and 320 mesh screens. The sand on the 200 & 320 mesh screens was determined by washing them onto a filter paper which was then dried and weighed. The results of these experiments expressed as percentage of sand removed are shown in Table 1. The equation 7 shows that

Table 1
Grit Removal $D_r = 2.54$ cm

Feed Concentration (100 - 200) mesh = 904 p.p.m.
(200 - 300) mesh = 104 p.p.m.

ΔH	R	E%		$\sqrt{\Delta H}\, R^{0.32}$
		100μ	60μ	
(meters)	%	100-200	200-320	$\sqrt{(\text{meter})}$
6.43	1.76	99.96	96.64	3.04
6.24	2.09	99.98	99.94	3.16
5.86	2.41	99.94	99.20	3.21
3.44	1.94	99.94	97.34	2.29
2.04	3.77	99.76	93.39	2.18
1.15	5.21	99.60	91.70	1.82
1.78	2.60	99.30	91.10	1.81
		s=60 cm/min	s=20 cm/min	
		d=100 microns	d=60 microns	

the pressure differential and percentage rejection are the important factors controlling the size of grit removable, i.e. S_{50}, and these factors are included in the table together with the function $\sqrt{\Delta H}\ R^{0.32}$ which is from equation 7. It was found that the sand on the 100 mesh screen had a mean particle size of 100 microns and should hence settle at a velocity of 60 cm/min and that the sand on the 320 mesh screen had a mean particle size of 60 microns and settling rate of 20 cms/min.

The hydrocyclone proved capable of virtually 100% removal of both grit sizes. The material left on the filter from the accepted sample appeared in most cases to be traces of paper fiber which may have been left in the casing of the pump and corners of the tank from their last usage.

We may hence say that since the 320 mesh sand is virtually 100% removed that the S_0 for this equipment on sand is less than 20 cm/min and that the S_{50} is less than 10 cm/min.

The predicted value from the previous report (Ref. 2) was a value of the order of 5 cm/min for S_{50} with a pressure drop of 6 meters of head and 10 cm/min for a pressure drop of 1.5 meters of head. This is not in conflict with the observation in Table 1.

3. Sawdust Separation

It was decided to do tests on removal of an organic material for two reasons:

a. To have some idea of capability of removing organics from sewage
b. To attempt to obtain an efficiency versus settling rate data, using screen analysis to separate sizes.

When attempts to obtain samples of granular plastic powder failed, the author was forced to fall back on the use of sawdust.

Bags of sawdust were obtained from a local lumber dealer and screened to obtain the finest materials which would pass through a 60 mesh screen. This fraction, which was only 10% of the sawdust, was then put in water and boiled to remove any air which would make it float. The wet sawdust was washed to remove resin then used in the tank for removal tests.

The laboratory procedure was similar to that used for the grit except that a 60 mesh screen was used above the 100 mesh screen. The results of these tests are shown in Table 2 together with the pressure drop, percent reject rate and their combined function.

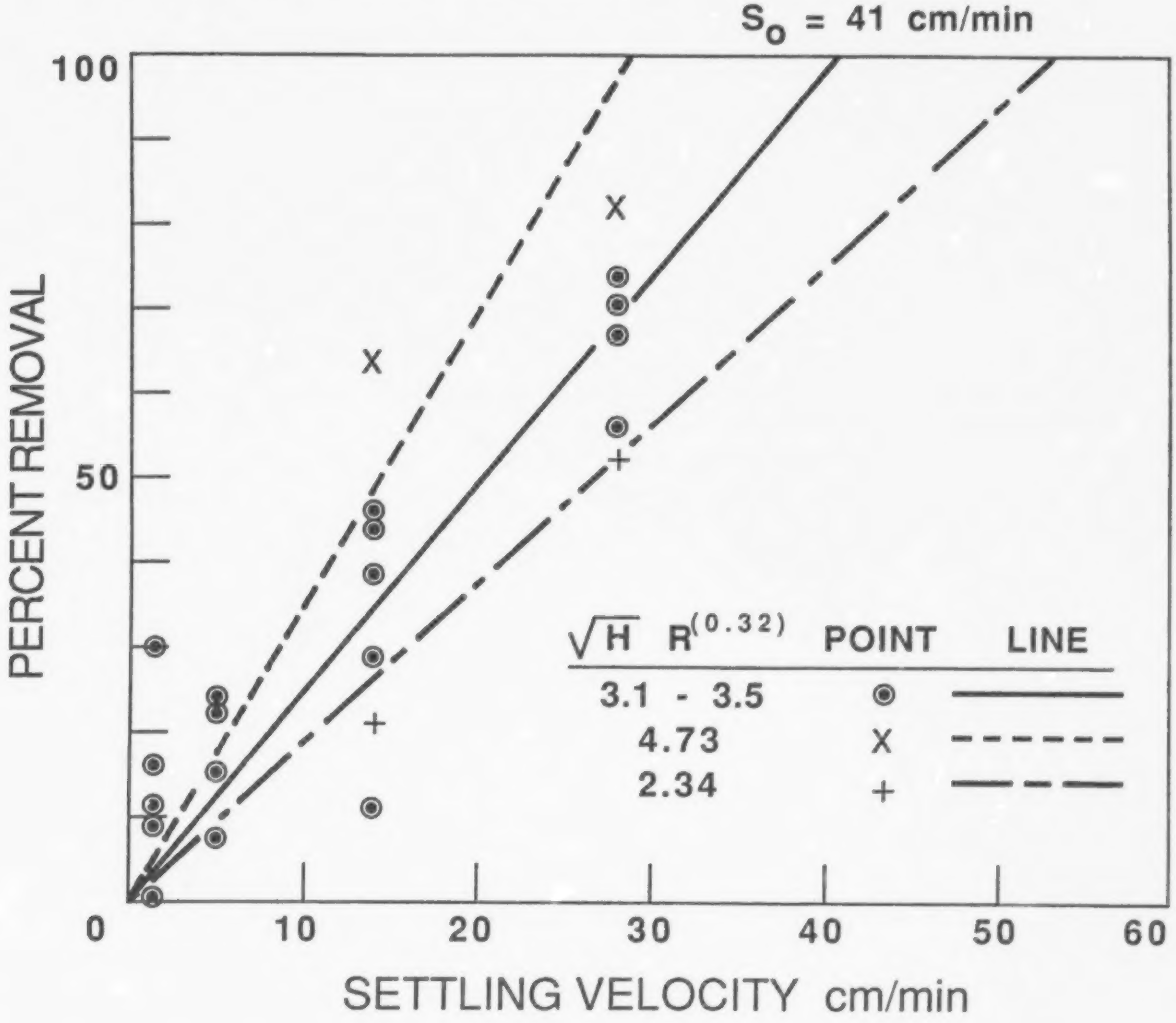
In order to express the screen mesh sizes or settling rates the density of the wetted sawdust particles was measured, using a picnometer, to yield a density of 1.1378 grams per ml. The net density of 0.1378 was then used with Stokes Law to give settling rates. The mean diameters of the various mesh fractions, their mean concentration in the feed and the expected settling rate of this material are shown at the top of Table 2.

Table 2

Sawdust Removal D = 2.54, 5.08, 3.81
Feed Concentration 60 mesh = 35 p.p.m.
100 mesh = 133 p.p.m.
200 mesh = 132 p.p.m.
325 mesh = 33 p.p.m.
Overall = 333 p.p.m.

Δ (meters)	R (%)	E%					$\sqrt{\Delta H}\ R^{(.32)}$
		60	100	200	325	All	
6.40	1.98	0	44.5	15.2	0	26.5	3.15
5.86	2.58	67.8	44.0	7.2	11.3	30.6	3.28
5.57	8.8	81.7	54.0	31.3	31.9	48.0	4.73
2.167	14.9	90.8	27.8	2.6	0	31.3	3.49
5.73	6.1	72.5	38.5	32.5	30.0	39.0	4.26
3.56	5.7	55.9	38.4	22.8	9.8	30.52	3.29
5.86	2.5	70.5	28.9	23.8	16.6	29.0	3.28
5.86	2.58	73.7	10.3				3.28
2.74	2.95	52.8	21.6				2.34
6.62	4.58	79.2	42.4				4.19
S	cm/min	28	14	5	1.5		
d	micron	250	176	100	55		

Figure 6 Efficiency in Removing Sawdust



There were 5 tests in which the separation product lies between 3.1 and 3.5 and the separation efficiency on the screen factors in these tests was plotted against the settling rates of the factors in Figure 6. These points, although showing considerable scatter, lay on a reasonable straight line in the form of the clarifier efficiency, i.e. equation 6. The condition with highest reject rate pressure product of 4.73 and lowest product of 2.34 are shown as other lines in Figure 6.

The value of S_0 from this graph, i.e., the 100% intercept, varied from 29.5 to 58.3 cms/min with the majority of test at 41.3 cms/min. This is much inferior to the results from grit tests which gave complete removal of grit with a settling rate of 20 cms/min. Close examination of the wetted sawdust showed that the particles were not granular but the majority were little flat chips with fragmented ends. The discrepancy is hence likely due to particle shape and removal efficiency of granular shaped organic particles would be higher.

4. Removal of Vegetable Washings

The liaison officer for the Ministry, Mr. Henry Kronis, arrived on Sept. 11 with a bag of vegetable washings for study. The sawdust had been cleaned out and this material was added to the tank. The vegetable washings consisted of black granular material, fibrous material and some slimy gelatinous material. Rejects from the hydrocyclone were very black but settling in Imhoff cones of feed and accepts showed only a small difference in settled volume. However these results may have little meaning as the fibrous and gelatinous material has great bulk, hence volume, and would not be removed. Attempts to filter the normal 10 1/2 liters of the feed led to blocking of the filter by the slimy material present. The sample sizes for filtrations were hence reduced to 500 c.c. with the results given below.

Test on September 11 Table 3

Sample	Concentration p.p.m.	Efficiency %
Feed	590	
Accept 1	362	38.6
Accept 2	352	40.34

The following day a 2" orifice was inserted to control reject flow and the hydrocyclone operated as follows.

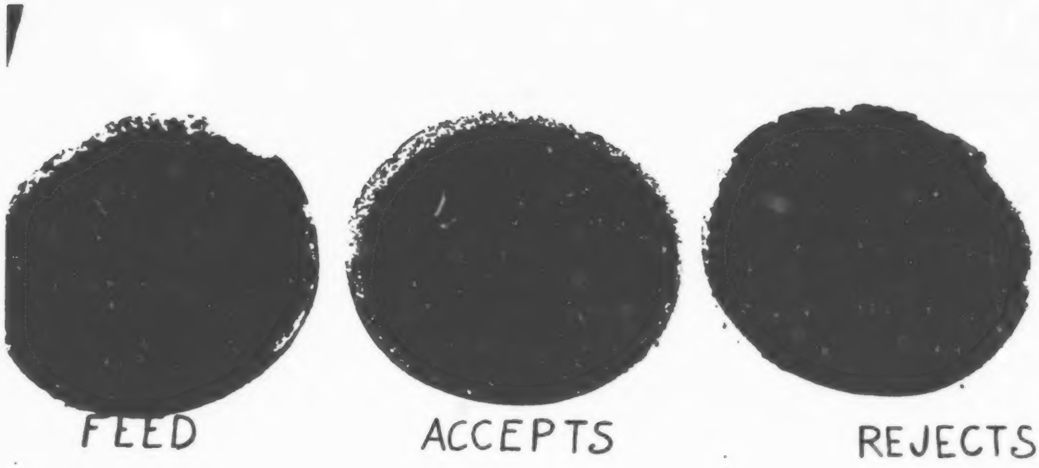


Figure 7 Filter Pads of Vegetable Washings

Pressure drop = 6.15 meters
Inlet Flow = 37 liters/second
Reject Flow = 4.25 liters/second
Rejection % = 11.486
Reject orifice = 2 inches or 5.08 cms

Samples were taken of feed accepts and rejects with results as follow:

Test on Sept. 12 Table 4

Sample	Concentration p.p.m.	Efficiency %
Feed	1746	
Accept	332	80.9
Rejects	5458	63.94

These results show much better performance than the previous day and, to show the character of materials in these filter pads and confirm this effective removal, they were photographed as shown in Figure 7.

Although the solids content of the three accepted samples are similar in the two days, there is a great discrepancy in the concentration in the feed sample. Efficiency can also be calculated by using the solids in the accepts and rejects, with their due proportion, to calculate a new feed and hence efficiency. This figure is shown on the rejects line of the results of September 12.

It would appear that there is a wide variation in the solids content of the feed with the use of a 500 c.c. sample. This is probably due to the imperfect blending of accepts and rejects by the stirrer as they proceed to the outlet. Hence the efficiency of 64%, calculated from accepts and rejects concentrations, is probably closest to the real efficiency. The calculated feed concentration from the joining of these two concentrations is 920 parts/million.

Further tests may be run on vegetable washings if the exact removal is important to a possible test of the hydrocyclone at Bradford.

Discussion and Conclusions

1. From experiments

The 25 inch hydrocyclone proved capable of handling a flow of 36.4 liters/second at a differential of 6 meters (or 600 US GPn at a differential of 20 feet). The inlet flow was not effected by the reject orifice size or outlet pressure, but by the differential only, according to an equation established by statistical analysis.

The reject flow was varied in experiments from 0.5 liters/second to 5 liters/second and was found to be dependent upon the reject orifice size and outlet pressure according to an equation also established by regression analysis. The percentage rejects can be obtained by use of both regression equations, equation 4, or the graphs, Figures 4 and 5.

The hydrocyclone proved capable of removing virtually all grit 60 microns in diameter or larger. It is believed that the unit may be able to remove 50% of grit which settles at a rate of 5 cm/minute.

The hydrocyclone separated fine organic matter, such as sawdust. It removed well over 50% of 60 mesh sawdust and 64% of the solids from vegetable washings. However, although granular shaped particles can readily be removed, fibers and large thin particles such as fruit and vegetable skinsmay be difficult to remove. Nevertheless the hydrocyclone has sufficient separating capability to be considered as a potential substitute for primary clarifiers. Overflow rates expressed as settling velocity for various devices are shown below in Table 5. It should be noted however that the velocity from the hydrocyclone has been established from experimental measurements, whereas the others are obtained using equation 5.

Separation Comparison Table 5

Device		Overflow rate cm/min.	m^3/m^2.day
Primary Clarifier	=	1 - 12	14 - 170
Hydrocyclone	=	10 - 40	140 - 570
Grit Channel	=	50 - 100	720 - 1440
Swirl Chamber	=	200 - 300	2880 - 4320

The hydrocyclone was designed with a high orifice ratio, i.e. smaller inlet and outlet sizes and hence lower flow for a given diameter. Whereas this might lead one to think that the unit tested would be uneconomic, since it would only handle about half the flow of a 25 inch (63.5 cm) unit of conventional design, this is false logic since one should only compare units which have similar separation capability. Based upon the author's own test data and promotional sales data on commercial hydrocyclones it would require a bank of 15 to 25 6 inch or 8 inch (15 - 20 cm) units to produce the separation capability and flow as obtained in these tests. These units would have small openings and would plug frequently from foreign objects in sewage. The author does not have financial data but it seems obvious that an installation of 15 - 8" hydrocyclone with headers, etc., should be much more expensive than one of the units under test.

2. Design

Experiments seem to have confirmed design prediction on hydraulics very well and have apparently also confirmed predictions on separation capability if one allows for the effect of shape.

It should hence be possible to extend the theory of scaling to produce other sizes of units in the same design proportions with reasonable confidence. The removal capability is probably much greater than needed for simple grit removal and a much larger unit with hydraulic capacity going up as the diameter squared would probably give adequate separation of grit. A unit 6 feet in diameter operating at 6 meters of head differential could probably handle 300 liters/second, and remove over 90% of 100 micron grit.

An alternative, for grit removal only, would be to increase the size of inlet and outlet passages to enable the 25 inch unit to handle a flow of 80 to 90 liters/second, at 6 meters differential, reducing the efficiency on 100 microns grit to approximately 90% efficiency from the existing 100%.

Better removal of organics would have been obtained by operating the existing design at a high pressure differential. It is designed to be able to withstand a static pressure of 25 p.s.i. and could hence be operated safely with this same differential, which would be 17 1/2 meters of water. The inlet flow, according to equation 1, would be 60.8 liters/second and the effective overflow rate as low as 6 cm/minute.

The unit is made of mild steel and is hence only suitable for a short test period, due to corrosion. In practice the corrosion problem may be overcome by rubber coating, as practiced by many manufactures of hydrocyclones for metallurgy, or of stainless steel or plastic as used in the paper industry. Very large units might be made of reinforced concrete with a ceramic lining.

3. Installations

It will usually require a bank of units to handle the sewage flow in a sewage plant. The number of units to be installed will depend on the maximum flow to be handled and the maximum pressure differential to be used in operation.

The hydrocyclones may be supplied either by gravity differential or by a pump. For pump supply, the best arrangement would probably be with the unit elevated and the outlet discharging to a high level between the accept and reject outlet, thus causing a slight vacuum at the outlet. For gravity operation the unit would need to have the inlet and outlet below the feed level and positioned such that the outlet flow discharges to a level somewhat between the accept and reject outlet.

The hydrocyclone can be operated with a broad range of pressure differentials and outlet pressures. However continuous operation is desirable as it requires several times the volume of the hydrocyclone to build up the velocity pattern, whereas on shutdown the contents all drain out through the rejects exit. A gradual build up of flow on start up and reduction in flow, such as achieved in slowly opening and closing a valve in the inlet line, is desirable to avoid water hammer effects.

Some form of automation may be necessary to look after the wide swing in flows normal to sewage plants. In a system with multiple primary units this may be looked after by shutting down numbers of units, by recirculating accepted flow for retreatment to keep the full system in operation or by varying the feed pressure. In a gravity feed system it may be possible to control the number of units in operation by allowing the level in the feed box to vary and having outlets from it to hydrocyclones at different levels. In systems with multiple pumps each pump could feed separate hydrocyclones units or banks of units.

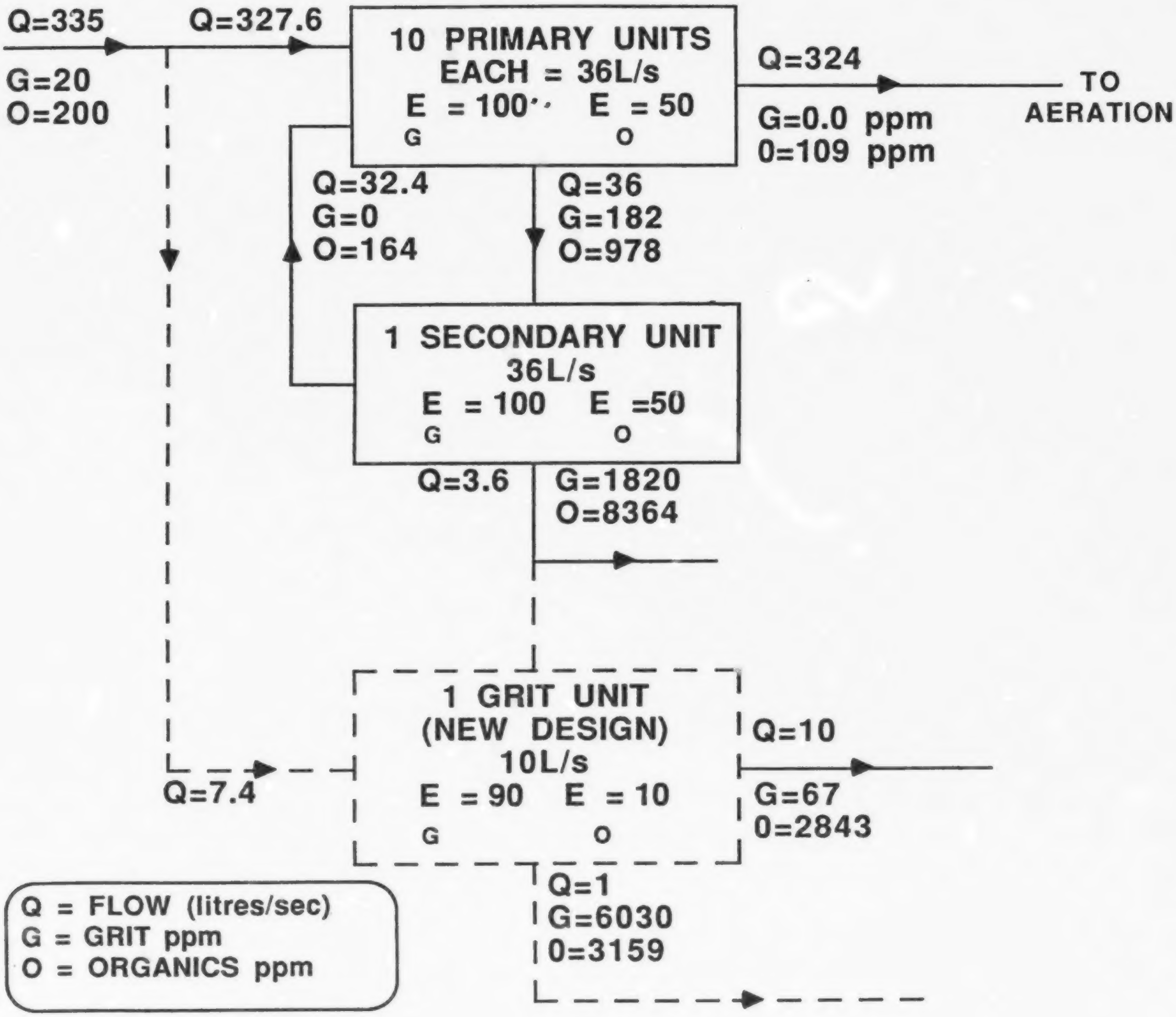
Every system must have a method of looking after the rejects from the primary bank of hydrocyclones. The system of secondary and tertiary banks of units used in the paper industry may be employed for this purpose. Figure 8 shows a flow chart showing how a system employed in place of a primary clarifier might operate. The logic of the system is also described below.

A. The system is designed to handle a maximum flow of 335 liters/second and it is assumed that the sewage contains 200 p.p.m. total organics and 20 p.p.m. grit. The primary system, consisting of 10 of the units tested operating at 6 meters of differential, handles 360 liters of input, rejects 10% of its input with 50% removal of organics and 100% removal of grit. The accepted flow of 324 liters/second goes to the aeration tank for secondary treatment while the rejects go to a secondary unit. The feed to the primary consists of the input plus the accepted flow from the secondary.

B. The secondary unit, of the same design, also operates at 6 meters of differential and 10% reject rate. It also would remove 100% of the grit, but since the organic is all the coarser material, it may remove 85%. The accepted flow would be returned for retreatment in the primary. The reject flow of 3.6 liters/second would have a grit concentration of 1,820 p.p.m. and organic content of 8,364 p.p.m. This material may then go to some thickening device and digestion.

C. It may be desirable to separate the grit from the organics in a third stage hydrocyclone. This would need to be a unit of lesser separating capability, by both design and operating pressure. It might be possible to obtain such a unit with 10% capability in removing the organics but 90% in removing grit. It would be necessary to dilute the rejects from the secondary with raw sewage to have sufficient flow to use a large enough unit that it would not block. The accepted flow of 10 liters/second would have only 67 p.p.m. of grit but 2,843 p.p.m. of organics and could be sent to some thickening device. The reject flow of 1 liter/second would have 6,030 p.p.m. of grit and 3,159 p.p.m. of organics. The latter organics would probably be

Figure 8 A Hydrocyclone System Schematic



coarser granular material such as coffee grounds or seeds which do not putrify and could go directly to landfill.

In a larger system, a third stage unit of high enough capacity could be used to build up final solids content in rejects to 2 to 3% solids (20,000 - 30,000 p.p.m.).

4. Application of Hydrocyclones

The hydrocyclone is a tool which has potential for use in environmental treatment in various roles, provided units are designed appropriately for the service.

The removal of grit is excellent and units could be employed either before or after screening to achieve superior grit removal. I would be preferable to use the hydrocyclones after screening to prevent possible blockage.

It is also possible to use hydrocyclones in place of primary clarifiers. It is particularly effective in removing granular materials and would be effective in such particles as sawdust, coffee grounds, seeds and undigested hard food particles such as corn kernels and nuts. The fluid shear would probably separate gas bubbles from particles which sometimes prevents settling in primary clarifiers.

However, separation in hydrocyclones is influenced by particle shape and particles with a large surface, such as fibres and skins, would be difficult to remove. Flocs of alum or ferric oxide from use of flocculents have large surface and would not be removed. On the other hand organic flocculents produce tighter flocs which might be removed by hydrocyclones.

The effect of replacing primary settling with hydrocyclones on the activated sludge process that follows is uncertain. We can speculate on the possible effects of removing granular particles but permitting fibrous and other high surface particles to pass on to the aeration tank. Microscopic examination of activated sludge usually shows that all fibrous particles are usually enclosed in colonies of bacteria. They may have the effect of producing a better settling sludge in the secondary clarifiers and thus permitting the process to run at a higher food to microorganism ratio.

In more recent years, municipal stormwater has been considered as contributing to environmental contamination. However, treating the entire volume of stormwater in sewage treatment plants raises difficult problems. One solution would be to pass the stormwater through an efficient hydrocyclone, with the reject portion being sent to sewage treatment.

Hydrocyclones may also be applied to solve pollution problems from industrial waste, by local treatment.

Although the research discussed here involved using hydrocyclones to remove particles denser than water, the author has also done research on use of hydrocyclones to remove oil and floating material from water. A copy of a report dealing with recent studies in this area will be sent to the liaison officer along with the report.

Recommendations

The hydrocyclone has performed well in pilot plant trials and is now ready for field trials.

The decision as to the location and nature of the field trial is one that must be made by the Ministry. The author would like the trial to be one where the equipment would be tested as a substitute for primary treatment. One form of application is where a plant is faced with treating an industrial waste which has fine granular material. The material from Bradford is an example of the type of problem where a hydrocyclone would be particularly useful. If further tests are needed to reach this decision, it would be preferable that they be carried out before May 1987, since next summer the Civil Engineering Department plans to make changes in the corner of the laboratory where the hydrocyclone pilot plant is located.

The original budget allowed funds for revision of the equipment after pilot studies and before field trials. Two such alterations might be rubber coating of the interior to reduce both abrasion and corrosion and construction of the curved cone and longer barrel alternative design shown in the original drawings. The decision on these matters will wait until the Ministry has read this report and made their recommendation as to what changes might be made.

References

1. Boadway, J.D. "A Low Pressure Hydrocyclone for Grit Removal", A report written for the Ministry of Environment.

2. Boadway, J.D. "A Hydrocyclone Designed for Energy Recover", A progress report written for the Ministry of Environment.

3. Boadway, J.D. "A Hydrocyclone Designed for Energy Recovery", A second Progress Report on Project No 184 PL.

4. Bradley, D. "The Hydrocyclone", a text published by Pergamon Press in 1965.

5. Freeman, H. and Skelton, Pulp and Paper Magazine of Canada 38 No. 2: 170-171, 188 (Convention issue 1937).

6. Hammer, Mark V. "Water and Wastewater Technology" page 355.

7. Field, Richard "The Dual Functioning Swirl Combined Sewer Overflow Regulator/Concentration", U.S. Environmental Protective Agency report PB-227-182, Sept. 1973.

8. Boadway, J.D. "Vortex Nozzles for Limitation of Discharge Rates", The Canadian Journal of Chemical Engineering Vol. 51, February 1973.

9. Medronho, R.A. and Svarovsky, L. "Tests to Verify Hydrocyclone Scale-up Procedure", Second International Conference on Hydrocyclones, Bath, England, Proceedings pages 1-14 (Sept 1984).

UPPER HUMBER RIVER
WATER QUALITY STUDY

TECHNICAL REPORT #8

A REPORT
OF THE

TORONTO AREA WATERSHED
MANAGEMENT STRATEGY
STEERING COMMITTEE

Prepared by:

Brian A. Hindley
Richard P. Hubbard
Stephen H. Maude

The Metropolitan Toronto and Region
Conservation Authority
5 Shoreham Drive
North York, Ontario
M3N 1S4

December, 1985

TABLE OF CONTENTS

Abstract

1.0 **Introduction**

2.0 **Methods**

- Study Area
- Surface Water Quality
- Bed Sediment Sampling
- Overland Sediment Delivery
- Field Inventory

3.0 **Results**

- Synoptic Survey
- Event Sampling: Comparisons to Water Quality Objectives
- Parameter Correlations
- Description of Wet Event
- Subbasin Chemical Loadings
- Bed Sediment Chemistry
- Land Use
- Overland Sediment Delivery
- Field Inventory

4.0 **Discussion**

5.0 **Conclusions and Recommendations**

- Conclusions
- Recommendations

6.0 **Literature Cited**

Abstract: During the course of the Toronto Area Watershed Management Strategy Study (TAWMS) it became apparent that violations of the Ontario Ministry of the Environment's Provincial Water Quality Objectives (PWQO) routinely occurred in the Humber River north of the Metropolitan Toronto boundary. This one year study was conducted to better identify and characterize the main sources of selected pollutant loadings within the predominantly rural Upper Humber River watershed. Grab samples were collected during three dry event periods between July and December 1984 as well as intensive sampling during one storm event which occurred in late fall. Fecal coliform geometric mean densities during dry weather indicated water quality degradation throughout the Upper Humber watershed, even at stations relatively close to source. Dry weather concentrations of other parameters including TSS, TP, Cu, Pb, and Cd were also in exceedance of PWQO at stations throughout the study area. Exceedances were particularly frequent between the towns of Bolton and Woodbridge. Identified point source inputs as well as stretches of severe streambank erosion and cattle access were all likely contributors to the observed parameter levels. The lowest dry weather concentrations generally occurred in December suggesting a strong seasonal influence. With some exceptions (notably Cu and Pb), parameter concentrations were greatest under wet weather conditions. Physiographic differences between subbasins, influencing both parameter concentrations and loadings during the storm event, were observed and are discusssed in the report. The study concludes that water quality problems on the Upper Humber watershed, although not of the magnitude of those occurring in the lower Humber, cannot be discounted in the development of a water management strategy if PWQO are to be achieved.

1.0 Introduction

The Toronto Area Watershed Management Strategy Study (TAWMS) was initiated in response to concerns expressed by the Metropolitan Toronto and Region Conservation Authority (MTRCA) and its member municipalities regarding the extent of water quality degradation in the watercourses and the lack of information on pollutant sources and remedies.

The purpose of the TAWMS study is to identify pollutant sources within the watersheds and develop a comprehensive water management plan which incorporates cost effective measures for improving water quality, and an implementation strategy which outlines agency responsibilities and time frames for improvement measures.

The five-year study emphasized the Mimico Creek, Humber and Don River watersheds since these typify the wide range of water quality problems experienced by all watersheds within the MTRCA jurisdiction. After an initial screening study in 1981, the TAWMS work schedule was to concentrate first on the Humber River and then develop strategies for the Don River and finally Mimico Creek.

Because of the complexity and greater significance of urban water quality problems and because of funding restraints, the intensive study of the Humber River in 1982 was limited to the watershed area within the Metropolitan Toronto boundaries. The study was again limited to the lower Humber River in 1983 when the resolution of water quality problems along the Metropolitan Toronto waterfront was added to the terms of reference for the TAWMS study.

As a result of detailed pollution studies on the lower Humber River from 1982-83, it became apparent that violations of the

MOE's Provincial Water Quality Objectives (PWQO) in the Humber River occurred north of the Metropolitan Toronto boundary. Therefore, in order to address the TAWMS objective of restoring water quality to PWQO, the incorporation of corrective measures in the Humber River north of the Metropolitan Toronto boundary was necessary as part of the overall strategy. Specifically, exceedances of fecal coliform bacteria (FC), total phosphorus (TP), total suspended solids (TSS), lead (Pb), cadmium (Cd) and copper (Cu) were of concern in the Upper Humber watershed (TAWMS 1984).

Accordingly, in 1984, the MTRCA submitted a proposal to the MOE and received a grant to address these concerns in the Upper Humber watershed. The specific objectives of this study were as follows:

1. To evaluate the contaminant contributions of Upper Humber River subbasins by sampling surface waters for selected chemical and microbiological parameters in dry and wet weather.

2. To sample the bed sediment of these same subbasins in order to obtain a more historical perspective on contaminant contributions.

3. To map areas of potentially high overland sediment delivery in rural areas of the watershed using an adaptation of the Universal Soil Loss Equation.

4. To identify and describe land use problems (e.g. livestock access), point source inflows and stream bank ercsion sites by inventorying watercourses of the Upper Humber River watershed.

2.0 Methods

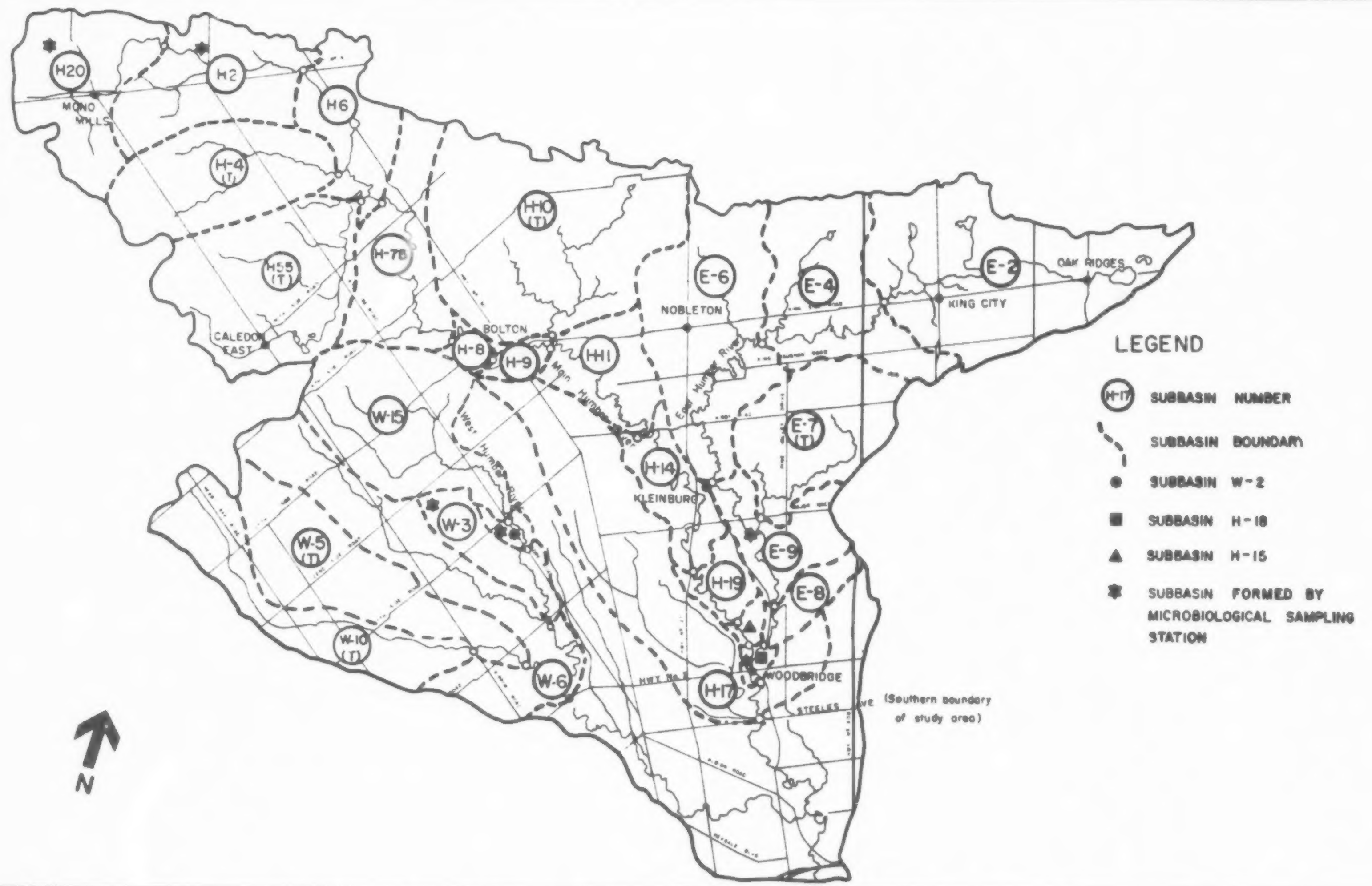
Study Area

The study area comprises 700 km^2 of the Humber River watershed north of Steeles Avenue, the Metropolitan Toronto boundary (Figure 1). The watershed is bounded by the communities of Oak Ridges to the northeast and Mono Mills to the northwest and is formed of three main rivers: the Humber, East and West Humber Rivers. Within the boundaries of the study area the Humber River is the largest of the three with a watershed area of 346 km^2. The East and West Humber Rivers have watershed areas of 190 and 160 km^2 respectively. Average stream gradients range from 1% in the upper reaches to 0.2% further downstream.

The study area is predominantly rural. The rural component (including areas of open space and forested lands) comprises about 97% of the watershed. Urban development is primarily restricted to several small communities found throughout the study area including Bolton, Nobleton, Woodbridge and Kleinburg.

Surface Water Quality

To assess the relative pollutant contributions of Upper Humber River subbasins a surface water quality monitoring network was established. Water quality sampling stations were set up at intervals along the Humber, East Humber and West Humber Rivers, and near the mouths of any major tributaries. Land use in the watershed was taken into consideration in the selection of the stations. For example, sampling stations were established to evaluate the effects of agricultural versus forested subbasins. Other stations were located upstream and downstream of urbanized areas such as the towns of Bolton and Woodbridge.



the metropolitan toronto and region conservation authority

MINISTRY OF THE ENVIRONMENT
TORONTO AREA WATERSHED MANAGEMENT STUDY TAWMS 85

UPPER HUMBER RIVER STUDY

SUBBASIN BOUNDARIES

FIGURE: 1

MARCH 1985

2 1 0 1 2 km

Synoptic Survey

Initially, 30 microbiological and 30 chemical stations were sampled synoptically to obtain some indication of where problem areas might exist. One sample for chemical analysis was taken from each station on June 20, 1984. Microbiological samples were taken daily from each station from June 20 to 22, 1984 inclusive.

Dry Event Sampling

Event sampling stations were selected based on the results of the synoptic survey. Although several new stations were created, the total number of sampling stations was reduced to 21 for microbiological sampling and 19 for chemical samples (Figure 1). Stage discharge curves were established at all chemical sampling stations from existing Water Survey of Canada (WSC) gauges or by installing staff gauges and monitoring flows. Three dry events were sampled between July 23 and December 13, 1984: Dry Event 1 from July 23 to 27, Dry Event 2 from August 27 to September 5, and Dry Event 3 from December 10 to 13. Dry event sampling consisted of taking chemical samples daily for three consecutive days (four days for Dry Event 2), and microbiological samples daily for five consecutive days (four days for Dry Event 3). At least two rainfree days were necessary prior to initiation of dry event sampling. Once sampling for a dry event had begun, however, precipitation could potentially interfere with the dry conditions. Dry Event 1 was completely free from rain. During Dry Event 2 it rained heavily prior to sampling on the third day. Therefore, sample days four and five were postponed until the following week after another two rain-free days had passed. An extra day of chemical sampling was added at this time. Rain also occurred just prior to the fourth day of sampling in Dry Event 3. These rain disturbances were taken into account in interpreting the dry weather data as outlined subsequently.

Wet Event Sampling

Wet event sampling was undertaken from November 11 to 14,1984. Three intense, short-duration rainfalls on November 9 and 10 preceded a major rain storm which occurred from late November 10 to November 11. For most stations, water samples were collected at 90-minute intervals throughout the initial runoff event.

At each chemistry station, river stage was recorded on every sampling occasion and a hydrograph was plotted. This hydrographic information was used to select about 6 samples from each station for analysis. For the tributary stations, H-4(T), H-55(T), H-10(T) and E-7(T), chemical samples taken throughout the initial runoff period were composited flow proportionately (Baun 1982).

Subsequent to the intensive sampling, additional samples were taken over the next three days as the rivers gradually returned to near base-flow conditions.

Sample Analysis

Water samples were analysed primarily for TSS, TP, Cu, Pb, Zn, Cd, FC, EC, FS and PA using standard MOE methods (MOE 1981). Sample analysis for Dry Event 3 was carried out by the Laboratory Services and Applied Research Branch of the MOE. All other samples were analysed by BEAK Consultants Ltd., by staff familiar with MOE analytical methods. We feel that some discrepancies in results obtained by the two laboratories may have occurred, particularly in the case of trace metals.

Bed Sediment Sampling

Bed sediment samples from 19 water chemistry stations were collected from November 20 to December 3, 1984. At each site, a composite of 3 samples was collected at river bends or where decreases in water velocity had permitted deposition of fine textured sediments. Samples were analysed for grain size, total phosphate, copper, lead, zinc and cadmium.

Overland Sediment Delivery

Sediment loading from rural overland sources was mapped using a methodology developed by the Lands Directorate at the Canada Centre for Inland Waters (CCIW) (Snell 1984). This methodology, an adaptation of the Universal Soil Loss Equation, utilizes a series of map overlays to target areas contributing significant overland sediment volumes to watercourses. While this technique does not quantify sediment inputs, it does allow for the setting of priority areas for management.

Field Inventory

A field inventory was conducted from June to October, 1984 in an effort to locate potential pollution sources. Two person crews walked watercourses of the Upper Humber system, noting problem land uses (e.g. areas where livestock had free access to the watercourse), point source inflows, and stream bank erosion sites. These features were described using standardized forms and their locations were indicated on topographic maps (1:25,000 or 1:50,000 scale).

3.0 Results

Drainage areas were planimetered for comparison to water chemistry loading calculations. Approximate areas for the 18 "chemistry" drainage basins are as follows:

1.3 - 10ha	H-15, H-9
10.1 - 30ha	H-14, H-11, H-4(T), E-8, W-10(T)
30.1 - 50ha	H-75, H-55(T), E-7, E-6, W-5(T), W-15
50.1 - 95ha	H-17, H-10(T), H-6, E-4, W-6

Locations of subbasins are shown in Figure 1.

Synoptic Survey

Fecal coliform analyses indicated fairly widespread exceedances of the Provincial Water Quality Objective of 100 counts/100 mls. Geometric mean densities ranged from 40 to 2,113, occurring at stations W-8 and E-8 respectively. The geometric means exceeded the objective at 19 of 30 stations. On the West Humber and Humber Rivers, exceedances occurred at 38% and 64% of the sampling stations respectively. All but one (88%) of the stations on the East Humber exceeded the objective. Escherichia coli densities closely paralleled those of fecal coliform bacteria.

The Provincial Water Quality Objectives (MOE 1984) state that when pathogenic organisms such as Pseudomonas aeruginosa can be enumerated and frequently isolated from water, a potential health hazard exists. Geometric mean densities of P. aeruginosa (PA) ranged from <2 which occurred at several stations to 12 on the West Humber at Highway 7 (W-6) and 10 on the Humber River at Steeles Avenue (H-17). The greatest densities generally occurred on the Humber River south of the community of Kleinburg.

Based on these results, some sampling stations were eliminated and others shifted to more adequately sample problem areas.

Concentrations of the nitrogen parameters (ammonia, total kjeldahl, nitrate and nitrite) were never in exceedance of suggested water quality guidelines. Similarly, zinc levels were well within the MOE objective of 0.05 mg/l at all stations. Based on these results samples were not analysed for the above parameters during the remainder of the study.

Total suspended solids exceeded the guideline of 25 mg/l (McNeely et al. 1979) at 12 of 30 stations. On the East Humber, the highest level (48 mg/l) was found at station E-8 near Woodbridge. On the West Humber the greatest concentration (98 mg/l) was found at station W-5(T) located on a tributary in the southern portion of the watershed. The highest overall TSS concentration of 124 mg/l was found at station H-14 on the Humber River. All five exceedances occurring on the Humber River were in the southern stretches of the watercourse.

Total phosphorus concentrations exceeded the guideline of 0.03 mg/l at 27 of 30 stations. Values ranged from 0.024 mg/l at E-8 and H-10(T) to 0.132 mg/l at H-14. The highest concentrations were found on the southern stretches of the Humber River above the town of Woodbridge.

Trace metal analyses for Cu, Pb and Cd revealed that wide-spread exceedances occurred only with Cu. Violations of the MOE objective occurred at 25 of 30 stations. Concentrations ranged from 0.003 mg/l at station H-4(T) to 0.021 mg/l at W-7(T). Although elevated Cu levels were found at W-7(T), the station was eliminated because of extremely low base flows and the strong likelihood that the tributary would become dry during summer periods. Analyses for Pb were maintained through the study because Pb concentrations were uniformly close to exceeding the objective throughout the watershed.

Event Sampling: Comparisons to Water Quality Objectives

At each sampling station, for each event, exceedances were considered in two ways: first, the frequency with which observed concentrations exceeded objectives or guidelines was tabulated, and, second, the degree to which observed concentrations exceeded objectives or guidelines was calculated. The degree of exceedance is presented as a "mean exceedance ratio". For chemical parameters, this was calculated as the arithmetic mean ratio of observed concentrations to the given objective or guideline. For fecal coliform bacteria the water quality objective is based on a geometric mean of samples collected. Therefore, the mean exceedance ratio for fecal coliforms was calculated as the ratio of the observed geometric mean fecal coliform count to the objective.

Fecal Coliforms (100 counts/100 ml; MOE 1984)

In general, EC counts were almost always over 90% of FC counts. Seventy-five percent and 87% of the FC values exceeded the objective for Dry Events 1 and 2 respectively. In contrast, during Dry Event 3 only 28% of the FC values exceeded the objective. For both the Wet Event and the wet portion of Dry Event 2, 98% of the FC values exceeded the objective.

In general, wet weather mean exceedance ratios were greater than dry weather mean exceedance ratios. Wet Event mean exceedance ratios were greater on the West Humber and East Humber Rivers than on the Humber River.

Fecal coliform levels immediately downstream of the towns of Woodbridge and Bolton (i.e. stations H-18, E-8 and H-9) were consistently higher than the FC levels of stations located just upstream from these communities.

Extremely high FC counts regularly occurred at stations H-2 and W-2.

In general FC:FS mean ratios were less than 4 during all events throughout the Humber watershed. Ratios greater than 4 consistently occurred at W-6 and W-5(T) in Dry Event 1 and at E-2 and H-2 in Dry Event 3. Ratios less than 0.5 consistently occurred at H-55(T) in Dry Event 1, at H-20 in Dry Event 2 and at E-9 and H-8 in Dry Event 3.

Pseudomonas aeruginosa (PA)

In general, PA counts tended to increase in subbasins with urban inputs. Dry and wet weather counts generally were greater than 10 below Bolton in the Humber, and in the East Humber upstream of E-4. However, PA counts in the West Humber were also high in the Wet Event. PA counts in Dry Event 3 were all generally less than 5.

Total Suspended Solids (25 mg/1; McNeely *et al.* 1979)

The TSS guideline was exceeded by 24%, 16% and 5% of the samples for Dry Events 1, 2 and 3 respectively. Exceedances occurred only in the lower portion of the watershed, and were limited to seven stations in Dry Event 1 (H-17, H-15, H-14 H-11 H-9, E-7(T), W-6), three stations in Dry Event 2 (H-17, H-15, H-14), and two stations in Dry Event 3 (H-15, H-14). Dry weather mean exceedance ratios were low.

Sixty-eight percent of samples collected during the wet portion of Dry Event 2 exceeded the guideline, as did 84% of samples collected during the Wet Event. With the exception of station H-55(T), wet weather exceedances occurred at all stations. Station H-55(T) was located immediately downstream of the swimming pond in Albion Hills Conservation Area; suspended particles likely settle in the pond before reaching the sampling station. Mean exceedance ratios for the wet portion of Dry Event 2 were generally greater than those recorded for the Wet Event; the greatest exceedances occurred in the lower stretches of the Humber River.

Total Phosphorus (0.03 mg/l; MOE 1984)

The percentage of samples which exceeded the TP guideline was 91% in Dry Event 1, 47% in Dry Event 2, and 19% in Dry Event 3. Ninety-seven percent and 94% of samples exceeded the guideline for the wet portion of Dry Event 2 and the Wet Event, respectively.

Dry weather mean exceedance ratios were uniformly low throughout the study area. As noted for TSS, TP mean exceedance ratios for the wet portion of Dry Event 2 were highest in the lower stretches of the Humber River and were generally greater than the TP mean exceedance ratios of the Wet Event.

Copper (0.005 mg/l; MOE 1984)

The Cu objective was exceeded in 98% and 82% of the samples for Dry Events 1 and 2 respectively. In contrast, no exceedances were recorded for Dry Event 3. During wet weather sampling the objective was exceeded in 92% and 88% of the samples for the wet portion of Dry Event 2 and the Wet Event respectively.

For all events except Dry Event 3, mean exceedance ratios were greater than one at all sampling stations. Generally these mean exceedance ratios were similar for both dry and wet weather samples, although some of the mean exceedance ratios during wet conditions were actually lower than those recorded for Dry events 1 and 2. This may indicate that dry weather sources of Cu were diluted in wet conditions.

Lead (0.025 mg/1; MOE 1984)

The Pb objective was never exceeded during Dry Event 3 and on only one occasion during Dry Event 1. In contrast, exceedances occurred in 71% of the samples during Dry Event 2; all stations except H-15 had at least one exceedance. Lower base flows during Dry Event 2 may have reduced the watershed's capacity to dilute Pb inputs resulting in higher Pb concentrations during this event.

Mean exceedance ratios were uniformly low throughout the watershed.

Parameter Correlations

Spearman rank correlation coeficients were calculated on the combined dry weather chemical data, and also on the event chemical data.

In dry weather, TDS and COND were positively correlated with Q and negatively correlated with TSS and Pb. Positive correlations occurred frequently between TSS and each of OP, TP, Cu and Pb, between Cu and each of OP, TP, and Pb, and between TP and OP.

Some changes in parameter correlations occurred in the Wet Event. Total suspended solids, OP, and TP became positively correlated with Q; OP, TP, and Cd exhibited more frequent correlations with TSS, whereas Cu and Pb correlations with TSS were less frequent. Copper and Pb were no longer negatively correlated with Q. Cadmium became positively correlated with Cu and Pb.

Description of Wet Event

For the purposes of the study, the Wet Event period encompassed six days, from November 9 to 14, 1984. The event was considered to run from 12:00 AM, Friday November 9 (0 hours) to 12:00 AM, Thursday November 15 (144 hours). To avoid possible confusion when comparing hydrographs or pollutographs from various stations, this six-day period will be hereafter referred to in terms of total event time (0 to 144 hours).

A total of 35mm of rain fell between the afternoon of November 9 and the early evening of November 11. The major portion of the event occurred between 42 and 66 hours (November 10 and 11), when 22 mm of rain fell. These heavy rains were preceded by three intense rainfalls of short duration.

A typical hydrograph is presented in Figure 2. On the figure, the period of rainfall in the study area, the flow event, and the sampled portion of the flow event is shown. The "flow event" was defined as the interval from the first rise in the hydrograph at that station until a return to near base flow when the final chemical samples were taken. The period of sampling indicated refers to chemical and microbiological sampling; not included are additional microbiological samples which were collected on November 14.

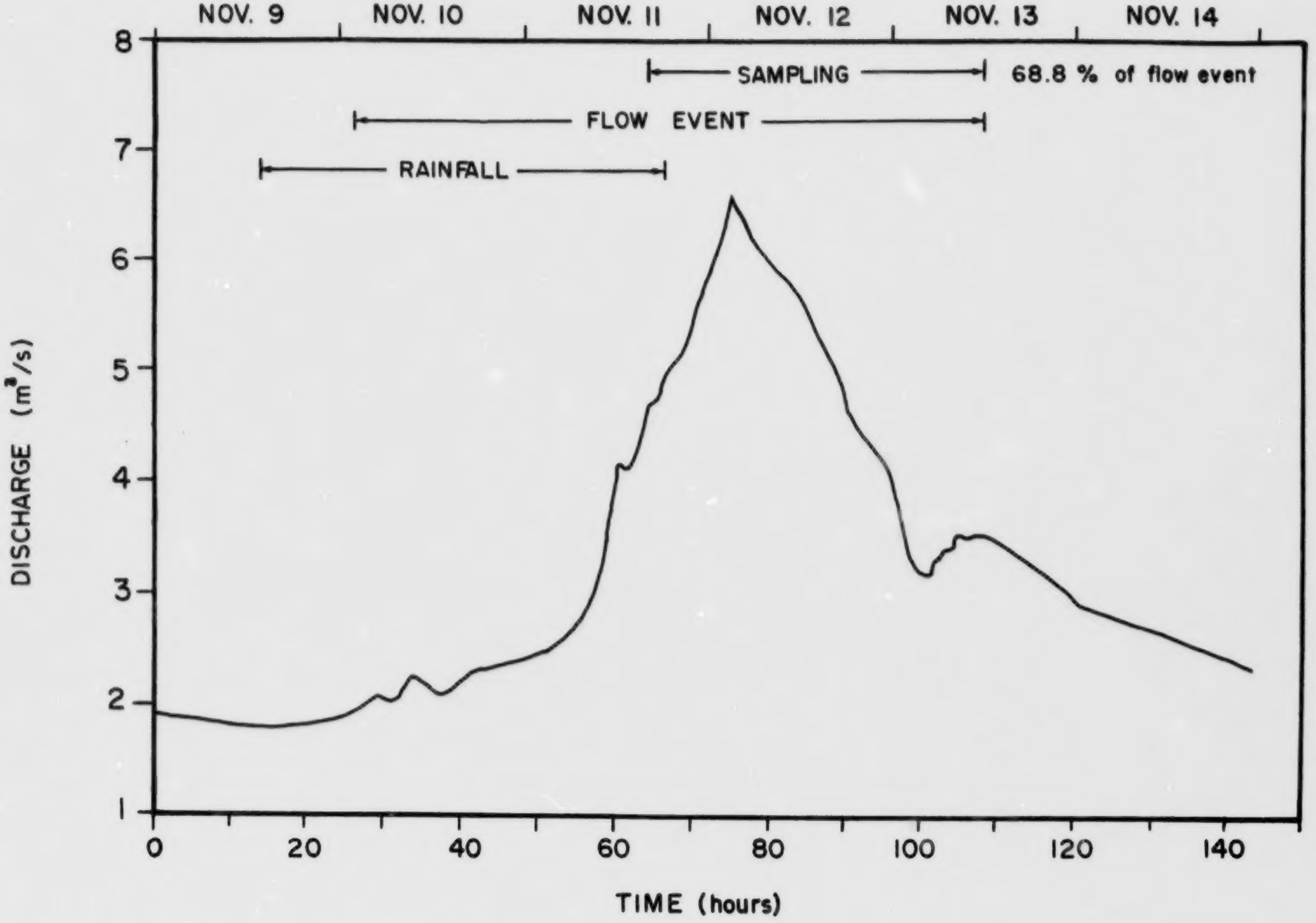
It can be seen from Figure 2 that, based on discharge, a significant percentage of the flow event was sampled. As previously mentioned, Wet Event chemical loads were defined as the total chemical mass that flowed out of a subbasin during the sampled portion of the event. Caution must be exercised in making comparisons of chemical loadings between stations because some spurious differences may occur if the portion of the flow event sampled was not exactly the same at each station. The hydrograph shown is more or less typical of all the sampling stations in that the peaks and falling portions of the hydrographs were sampled.

"Pollutographs", plots of chemical concentrations versus time, were plotted for stations at the confluence of each of the 3 tributaries. At station E-8 the concentrations of TSS, TP, Cu, Pb and Cd all closely paralleled discharge. At station H-14 parameter concentrations also paralleled discharge, although Cd and Cu concentrations increased again approximately 15 hours after the hydrographic peak. Compared to stations H-14 and E-8, obvious differences occurred in the temporal pattern of contaminant inputs at station W-6. At this station the peak concentrations of TSS TP Cu Pb and Cd all preceded the hydrographic peak by at least 10 hours. This suggests that, in terms of contaminant inputs at station W-6, the initial runoff period is of greatest significance.

It is interesting to note the close association of TSS and TP in all of the examples. The implication is that phosphorus is largely sediment-transported. A similar association may exist between TSS and metals, however, the pollutographs indicate that some departures from this occur.

Subbasin Chemical Loadings

For each event the mean chemical contributions (i.e. discharge (Q), TSS, TP, Cu, Pb, Cd) of the subbasins were displayed on schematic diagrams of the Upper Humber watershed. Subbasin chemical contributions were represented as percentages of the loadings at the "mouth" of the Upper Humber watershed, the "mouth" being defined as the southern-most boundary of the study area. As the confluence of the West Humber River with the Humber River is downstream of the study area boundary (Figure 1) it was necessary to consider the West Humber separately from the Humber



the metropolitan toronto and region conservation authority

MINISTRY OF THE ENVIRONMENT
TORONTO AREA WATERSHED MANAGEMENT STUDY

UPPER HUMBER RIVER STUDY

SAMPLING STATION H-14
WET EVENT HYDROGRAPH

FIGURE: 2

MARCH 1985

and East Humber Rivers. Therefore, subbasin chemical loadings were expressed as a percentage of the loading at Highway 7 (station W-6) for the West Humber River stations, and as a percentage of the loading at Steeles Avenue (station H-17) for all other stations. Obviously it was possible in some instances for the subbasin loadings of certain parameters to exceed those ocurring at the "mouth". In those cases the subbasin loading percentages were recorded as values greater than 100%.

Chemical loadings by subbasin are presented in Figures 3 to 7 and Tables 1 to 5 and are discussed below.

Total Suspended Solids

Dry weather TSS contributions were minimal from the Humber River upstream of the Albion Hills. Although subbasin H-6 accounted for just over 50% of the Upper Humber River's dry weather discharge, it contributed less than 15% of the TSS load. Similarly, the tributaries "Coffey Creek" (H-4(T)), Centreville Creek (H-55(T)),and Cold Creek (H-10(T)) contributed little to the total TSS load. In Dry Events 1 and 2 there was an increase in TSS loading through the town of Bolton, although this trend was reversed in Dry Event 3. The greatest dry weather contributions of TSS occurred downstream of Bolton within subbasins H-11, H-14, and especially H-15. The East Humber River acted as relatively clean dilution for the Humber River at Woodbridge.

Relative to the Humber River, the West Humber River's dry weather discharge is minimal (≤10% of the Humber River's discharge); the river becomes intermittent in summer. The West Humber River upstream of subbasin W-15 contributed virtually nothing to the system in dry weather. In terms of TSS, "Gore Creek" (subbasins W-5(T) and W-10(T)) likewise contributed minimally in dry weather.

Relative subbasin contributions of the Humber River did not change appreciably during the wet portion of Dry Event 2. On the West Humber River, however, there was a marked increase in the relative TSS loading of subbasin W-5(T).

During the Wet Event there was an increase in the relative TSS contribution from the H-6 subbasin. Again there was an increase in TSS load through the town of Bolton, however the relative contributions of subbasins H-11, H-14, and H-15 were lower than in dry weather. In general, the Humber River upstream of Woodbridge accounted for a smaller proportion of the total discharge than it had in dry weather - only 50% in the wet event compared with 70 to 80% in dry weather. The relative contribution of the East Humber River to total discharge was also reduced. This indicates the increased importance of subbasin H-17 in the Wet Event. This trend was not evident in the wet portion of Dry Event 2, suggesting that there may be differences in the way the watershed responds to various storm events.

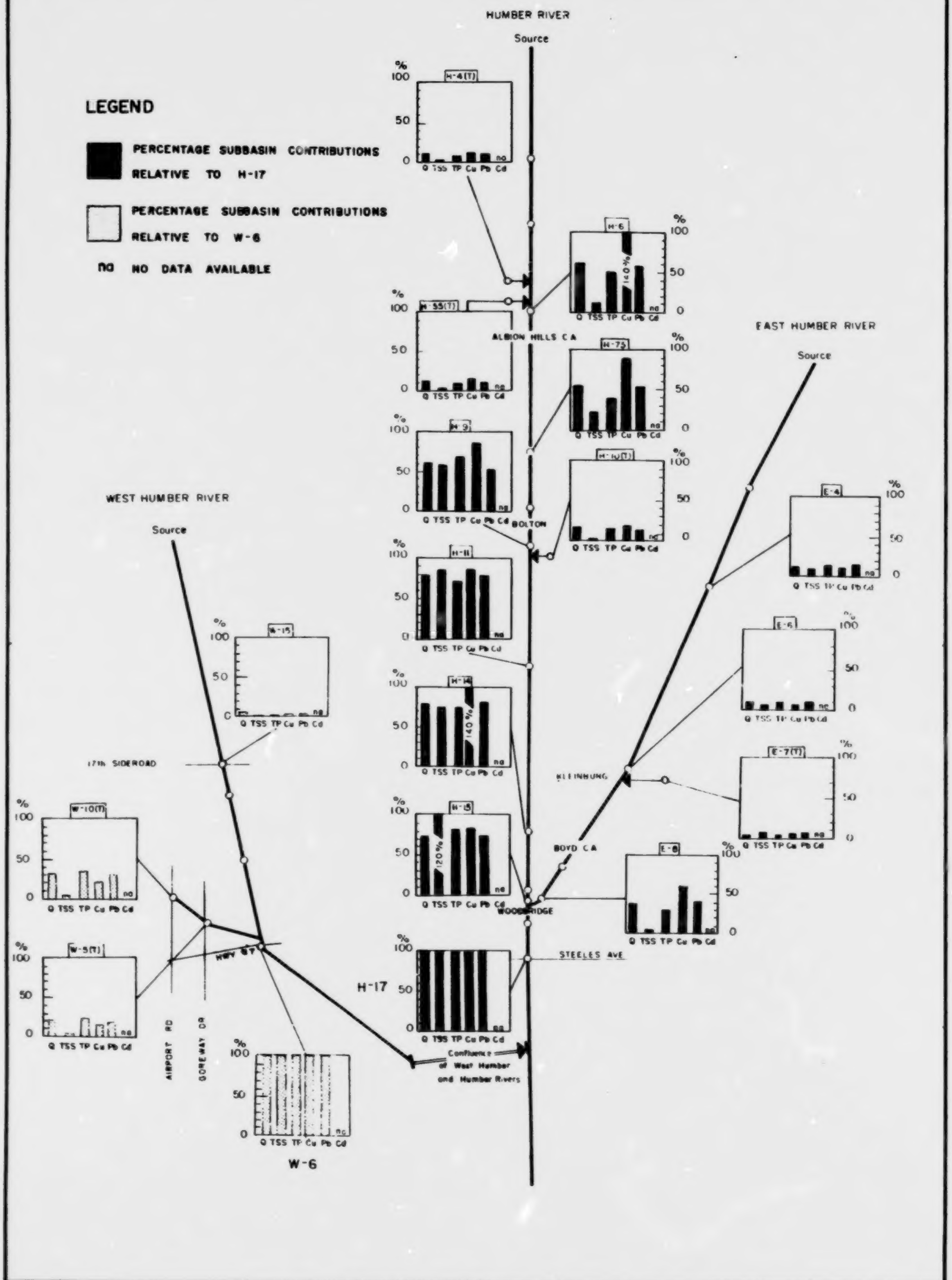
On the West Humber River, the major TSS inputs during the Wet Event occurred within the W-6 subbasin; as in dry weather, the other subbasins contributed relatively little to the total TSS load. In the Wet Event, the discharge of the West Humber River relative to the Humber River increased to 33%. Relative impacts of the two rivers on the lower Humber are hard to determine based on our data because the West Humber River passes through Claireville Reservoir between station W-6 and its confluence with the Humber River near Weston Road.

Total Phosphorus

Total phosphorus contributions varied considerably between Dry Events 1, 2 and 3. Exceptions were the relative loadings from the upstream Humber River tributaries H-4(T), H-55(T) and

Table 1: **Mean Instantaneous Loadings and Mean Concentrations - Dry Event 1.**

	Parameter									
			TSS		TP		Cu		Pb	
Station	Cumulative Drainage Area (sq. km)	Discharge (cu. m/s)	Loading (mg/s)	Conc. (mg/l)	Loading (mg/s)	Conc. (mg/l)	Loading (mg/s)	Conc. (mg/l)	Loading (mg/s)	Conc. (mg/l)
H-17	540	1.41	36067	25.58	84.8	0.060	15.1	0.011	26.4	0.019
H-15	290	1.07	43229	40.40	70.8	0.066	12.6	0.012	19.3	0.018
H-14	281	1.12	27000	24.11	64	0.057	21	0.019	21	0.019
H-11	268	1.13	30977	27.41	60.5	0.054	13.2	0.012	20.7	0.018
H-10(T)	63	0.24	1927	8.03	14.4	0.060	3.04	0.013	4.09	0.017
H-9	188	0.88	22168	25.19	58.8	0.067	13	0.015	14.2	0.016
H-75	177	0.77	7556	9.81	34.2	0.044	13.7	0.018	13.5	0.018
H-6	146	0.85	4278	5.03	42.8	0.050	21.2	0.025	14.6	0.017
H-55(T)	44	0.16	1264	7.90	8.26	0.052	2.24	0.014	2.58	0.016
H-4(T)	23	0.16	827	5.17	6.59	0.041	2.24	0.014	2.72	0.017
E-8	194	0.56	2992	5.34	26.2	0.047	9.33	0.017	11.3	0.020
E-7(T)	35	0.077	2549	33.10	4.64	0.060	0.87	0.011	1.68	0.022
E-6	141	0.14	2833	20.24	10.4	0.074	0.9	0.006	2.63	0.019
E-4	95	0.18	3721	20.67	12.4	0.069	2.18	0.012	3.81	0.021
W-6	143	0.088	2460	27.95	5.9	0.067	1.78	0.020	1.65	0.019
W-5(T)	59	0.02	108	5.40	1.52	0.076	0.29	0.015	0.35	0.018
W-10(T)	21	0.028	119	4.25	1.85	0.066	0.41	0.015	0.5	0.018
W-15	32	0.0037	10	2.70	0.073	0.020	0.069	0.019	0.056	0.015



the metropolitan toronto and region conservation authority

MINISTRY OF THE ENVIRONMENT

TORONTO AREA WATERSHED MANAGEMENT STUDY 85

UPPER HUMBER RIVER STUDY

FIGURE 3

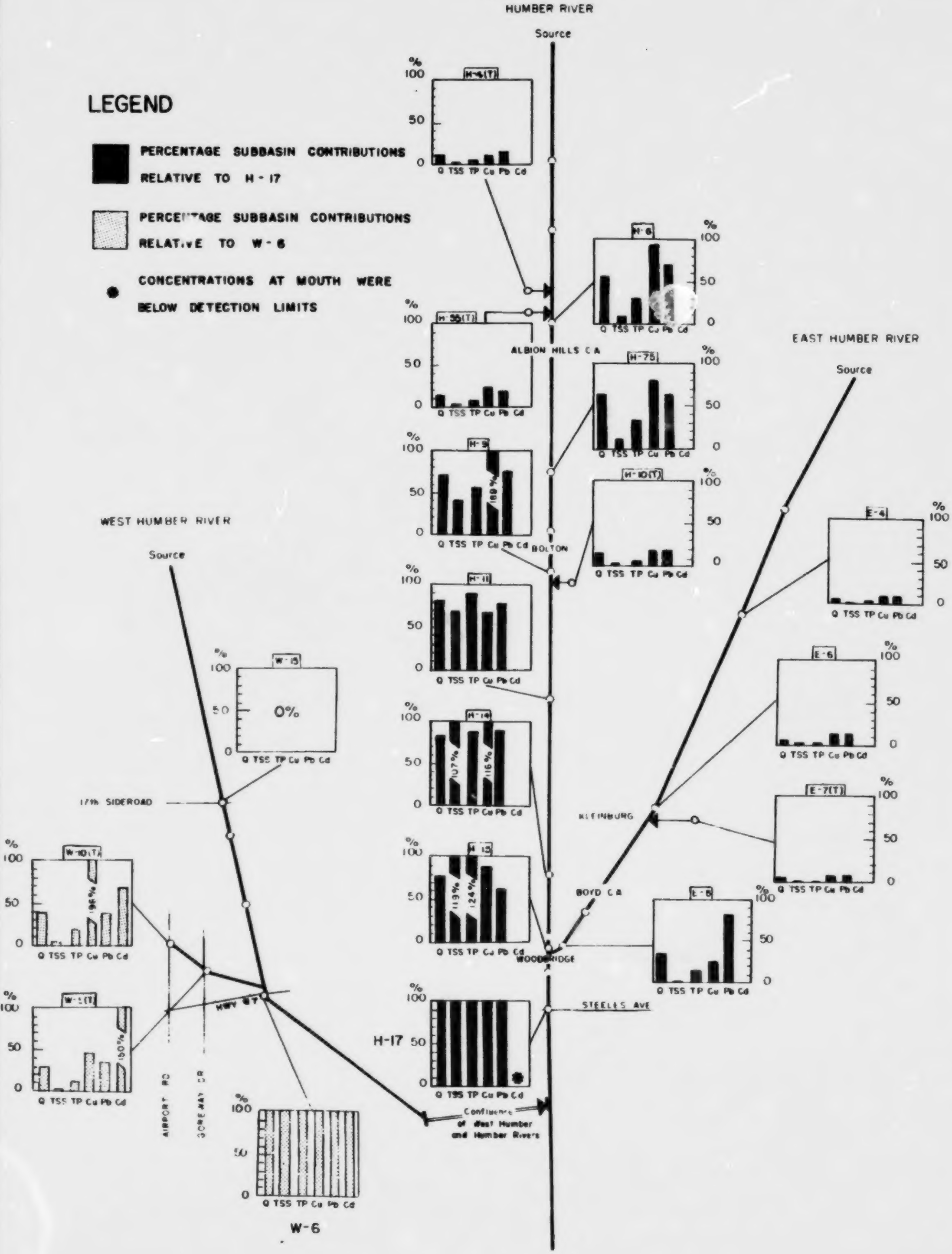
CHEMICAL LOADINGS BY SUBBASIN
DRY EVENT I

MARCH 1985

2 0 2 km

Table 2: Mean Instantaneous Loadings and Mean Concentrations - Dry Event 2.

	Parameter									
			TSS		TP		Cu		Pb	
Station	Cumulative Drainage Area (sq. km)	Discharge (cu. m/s)	Loading (mg/s)	Conc. (mg/l)	Loading (mg/s)	Conc. (mg/l)	Loading (mg/s)	Conc. (mg/l)	Loading (mg/s)	Conc. (mg/l)
H-17	540	1.22	34800	28.52	66.6	0.055	9.47	0.008	29.4	0.024
H-15	290	0.97	41299	42.58	82.4	0.085	8.31	0.009	18.5	0.019
H-14	281	1.01	37100	36.73	59	0.058	11	0.011	26	0.026
H-11	268	0.98	23628	24.11	59.2	0.060	6.63	0.007	22.7	0.023
H-10(T)	63	0.22	1220	5.55	4.63	0.021	1.82	0.008	5.64	0.026
H-9	188	0.85	14091	16.58	38.8	0.046	18.6	0.022	22.2	0.026
H-75	177	0.77	4252	5.52	23.6	0.031	7.73	0.010	18.6	0.024
H-6	146	0.69	3105	4.50	20	0.029	9.14	0.013	21.4	0.031
H-55(T)	44	0.17	1276	7.51	5.85	0.034	2.29	0.013	5.8	0.034
H-4(T)	23	0.13	976	7.51	3.84	0.030	1.14	0.009	4.57	0.035
E-8	194	0.46	2295	4.99	9.78	0.021	2.63	0.006	23.7	0.052
E-7(T)	35	0.073	584	8.00	1.02	0.014	0.74	0.010	3.14	0.043
E-6	141	0.33	1102	3.34	2.45	0.007	1.21	0.004	3.66	0.011
E-4	95	0.073	292	4.00	1.63	0.022	0.83	0.011	2.71	0.037
W-6	143	0.08	1680	21.00	4.16	0.052	0.56	0.007	2.64	0.033
W-5(T)	59	0.024	23	0.96	0.41	0.017	0.26	0.011	0.92	0.038
W-10(T)	21	0.03	103	3.43	0.83	0.028	1.1	0.037	1.03	0.034
W-15	32	0	0	0.00	0	0.000	0	0.000	0	0.000



the metropolitan toronto and region conservation authority

MINISTRY OF THE ENVIRONMENT

TORONTO AREA WATERSHED MANAGEMENT STUDY 85

UPPER HUMBER RIVER STUDY

FIGURE 4

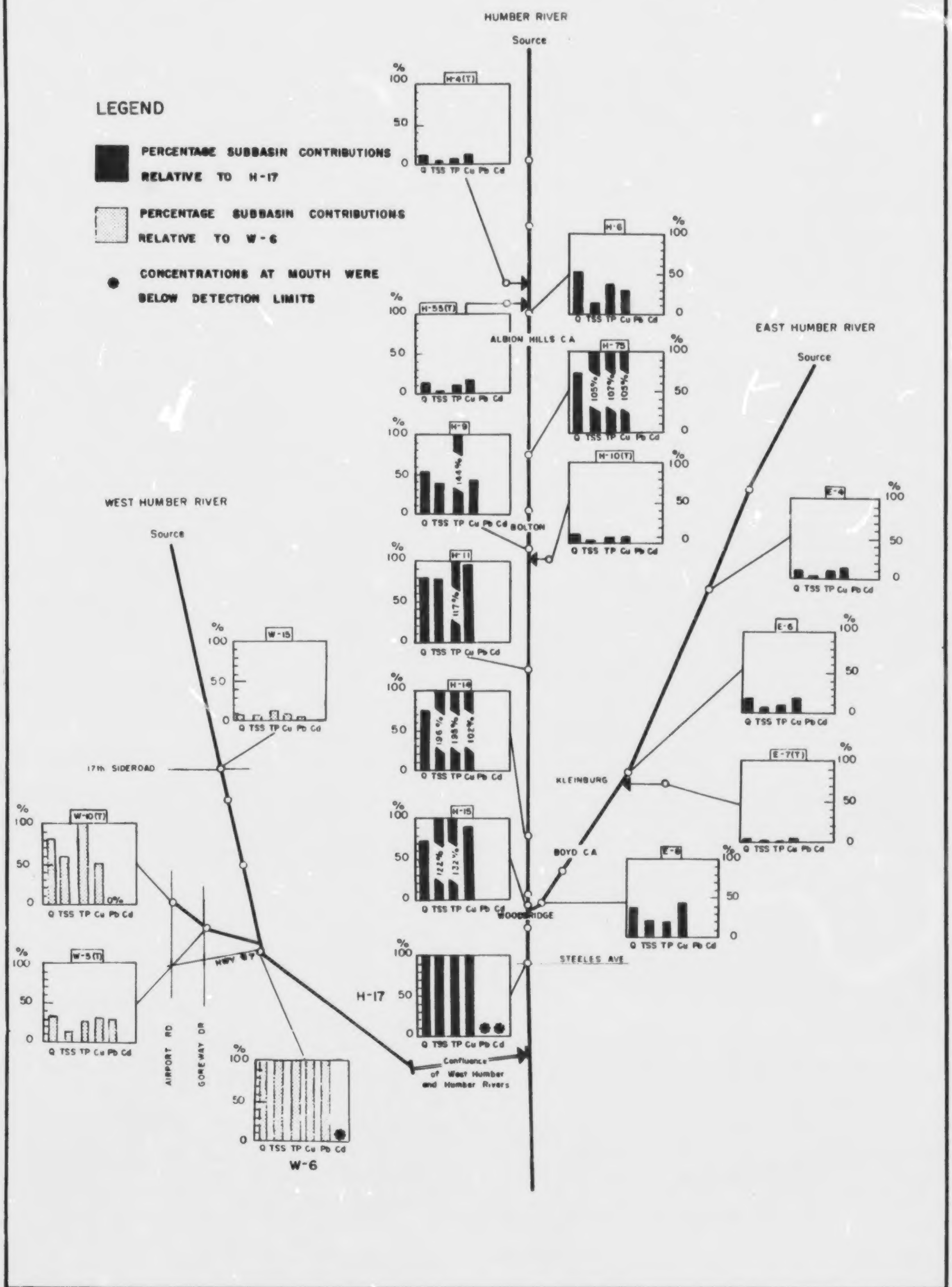
CHEMICAL LOADINGS BY SUBBASIN
DRY EVENT 2 (DRY PORTION)

MARCH 1985

2 1 0 1 2 km

Table 3: Mean Instantaneous Loadings and Mean Concentrations - Dry Event 3.

	Parameter									
			TSS		TP		Cu		Pb	
Station	Cumulative Drainage Area (sq. km)	Discharge (cu. m/s)	Loading (mg/s)	Conc. (mg/l)	Loading (mg/s)	Conc. (mg/l)	Loading (mg/s)	Conc. (mg/l)	Loading (mg/s)	Conc. (mg/l)
H-17	540	2.36	23512	9.96	40.9	0.017	3.95	0.002	0	0.000
H-15	290	1.76	28676	16.29	54.2	0.031	3.59	0.002	0	0.000
H-14	281	1.76	46100	26.19	80	0.045	4	0.002	0	0.000
H-11	268	1.88	18591	9.89	47.6	0.025	3.77	0.002	0	0.000
H-10(T)	63	0.3	1082	3.61	3.43	0.011	0.3	0.001	0	0.000
H-9	188	1.24	9014	7.27	59.4	0.048	1.63	0.001	0	0.000
H-75	177	1.78	24738	13.90	43.8	0.025	4.14	0.002	0	0.000
H-6	146	1.25	3030	2.42	16.3	0.013	1.25	0.001	0	0.000
H-55(T)	44	0.3	757	2.52	4.09	0.014	0.6	0.002	0	0.000
H-4(T)	23	0.27	730	2.70	2.87	0.011	0.45	0.002	0	0.000
E-8	194	0.92	4723	5.13	8.26	0.009	1.84	0.002	0	0.000
E-7(T)	35	0.1	482	4.82	0.52	0.005	0.17	0.002	0	0.000
E-6	141	0.43	1818	4.23	4.13	0.010	0.73	0.002	0	0.000
E-4	95	0.26	767	2.95	4.16	0.016	0.53	0.002	0	0.000
W-6	143	0.26	1126	4.33	2.64	0.010	0.81	0.003	0.64	0.002
W-5(T)	59	0.09	155	1.72	0.66	0.007	0.27	0.003	0.19	0.002
W-10(T)	21	0.21	659	3.14	2.6	0.012	0.41	0.002	0	0.000
W-15	32	0.022	80.9	3.68	0.33	0.015	0.066	0.003	0.033	0.002



the metropolitan toronto and region conservation authority

MINISTRY OF THE ENVIRONMENT

TORONTO AREA WATERSHED MANAGEMENT STUDY 85

UPPER HUMBER RIVER STUDY

FIGURE 5

CHEMICAL LOADINGS BY SUBBASIN
DRY EVENT 3

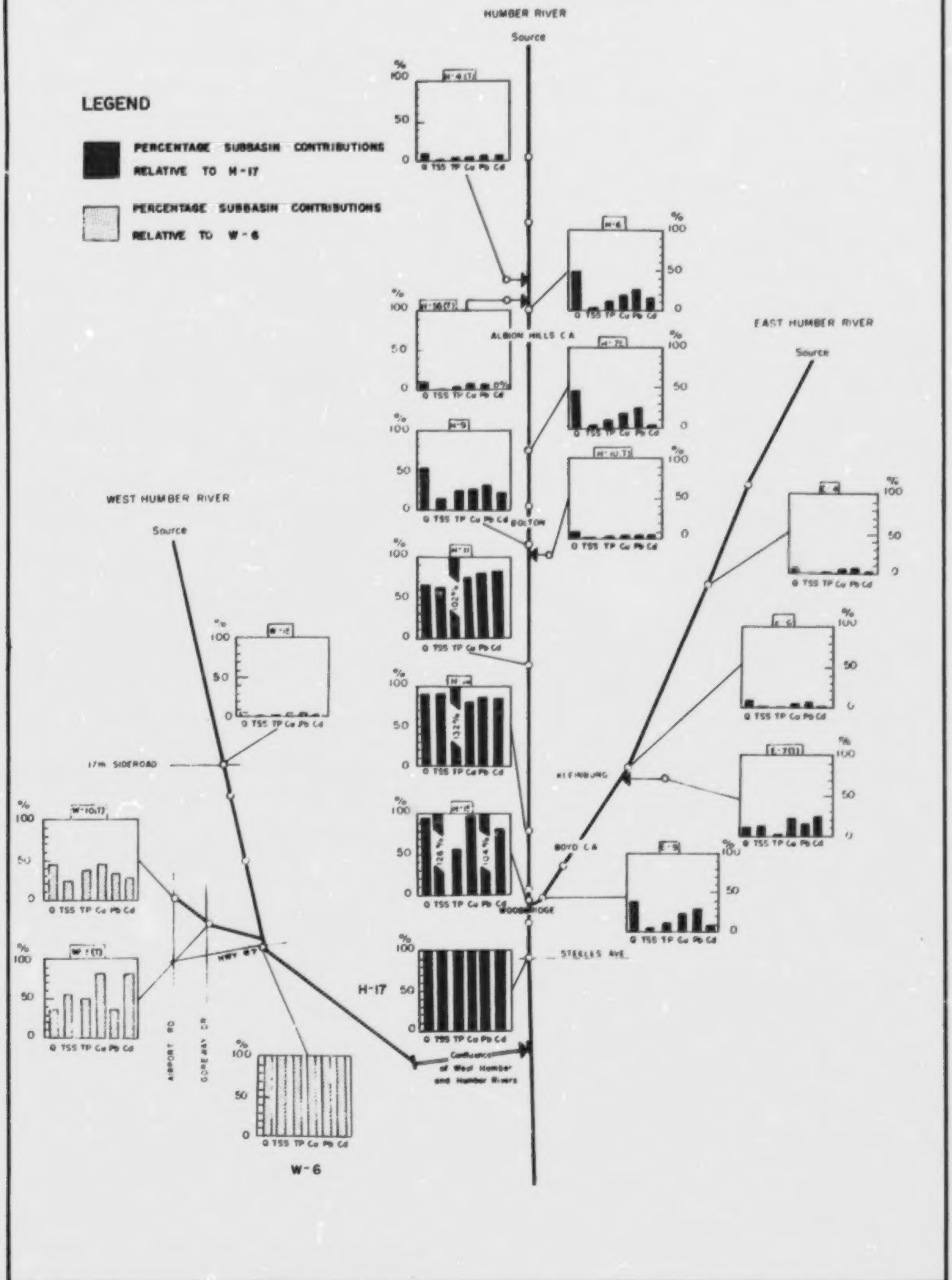
MARCH 1985

2 1 0 1 2 km

Table 4: Mean Instantaneous Loadings and Mean Concentrations - Dry Event 2 (wet portion).

Parameter

Station	Cumulative Drainage Area (sq. km)	Discharge (cu. m/s)	TSS		TP		Cu		Pb	
			Loading (g/s)	Conc. (mg/l)	Loading (g/s)	Conc. (mg/l)	Loading (g/s)	Conc. (mg/l)	Loading (g/s)	Conc. (mg/l)
H-17	540	3.62	1574700	435.00	1180	0.326	90	0.025	253	0.070
H-15	290	3.48	1989400	571.67	694	0.199	90	0.026	255	0.073
H-14	281	3.24	1417000	437.35	1560	0.481	74	0.023	220	0.068
H-11	268	2.34	971000	414.96	1200	0.513	69	0.029	195	0.083
H-10(T)	63	0.39	22100	56.67	35	0.090	3.8	0.010	15	0.038
H-9	188	1.91	249000	130.37	274	0.143	23	0.012	78	0.041
H-75	177	1.71	51000	29.82	118	0.069	16	0.009	62	0.036
H-6	146	1.78	61700	34.66	143	0.080	16	0.009	66	0.037
H-55(T)	44	0.44	3390	7.70	36	0.082	5.8	0.013	15	0.034
H-4(T)	23	0.38	39700	104.47	60	0.158	4.4	0.012	15	0.039
E-8	194	1.42	98900	69.65	130	0.092	20	0.014	75	0.053
E-7(T)	35	0.4	200900	502.25	41	0.103	19	0.048	45	0.113
E-6	141	0.33	23700	71.82	17	0.052	3.3	0.010	18	0.055
E-4	95	0.31	18400	59.35	14	0.045	4.3	0.014	18	0.058
W-6	143	0.42	71400	170.00	75	0.179	7.1	0.017	20	0.048
W-5(T)	59	0.15	39600	264.00	38	0.253	5.9	0.039	7.6	0.051
W-10(T)	21	0.18	17900	99.44	28	0.156	3.3	0.018	6.7	0.037
W-15	32	0.018	124	6.89	0.57	0.032	0.34	0.019	0.72	0.040



the metropolitan toronto and region conservation authority

MINISTRY OF THE ENVIRONMENT

TORONTO AREA WATERSHED MANAGEMENT STUDY 85

UPPER HUMBER RIVER STUDY

CHEMICAL LOADINGS BY SUBBASIN
DRY EVENT 2 (WET PORTION)

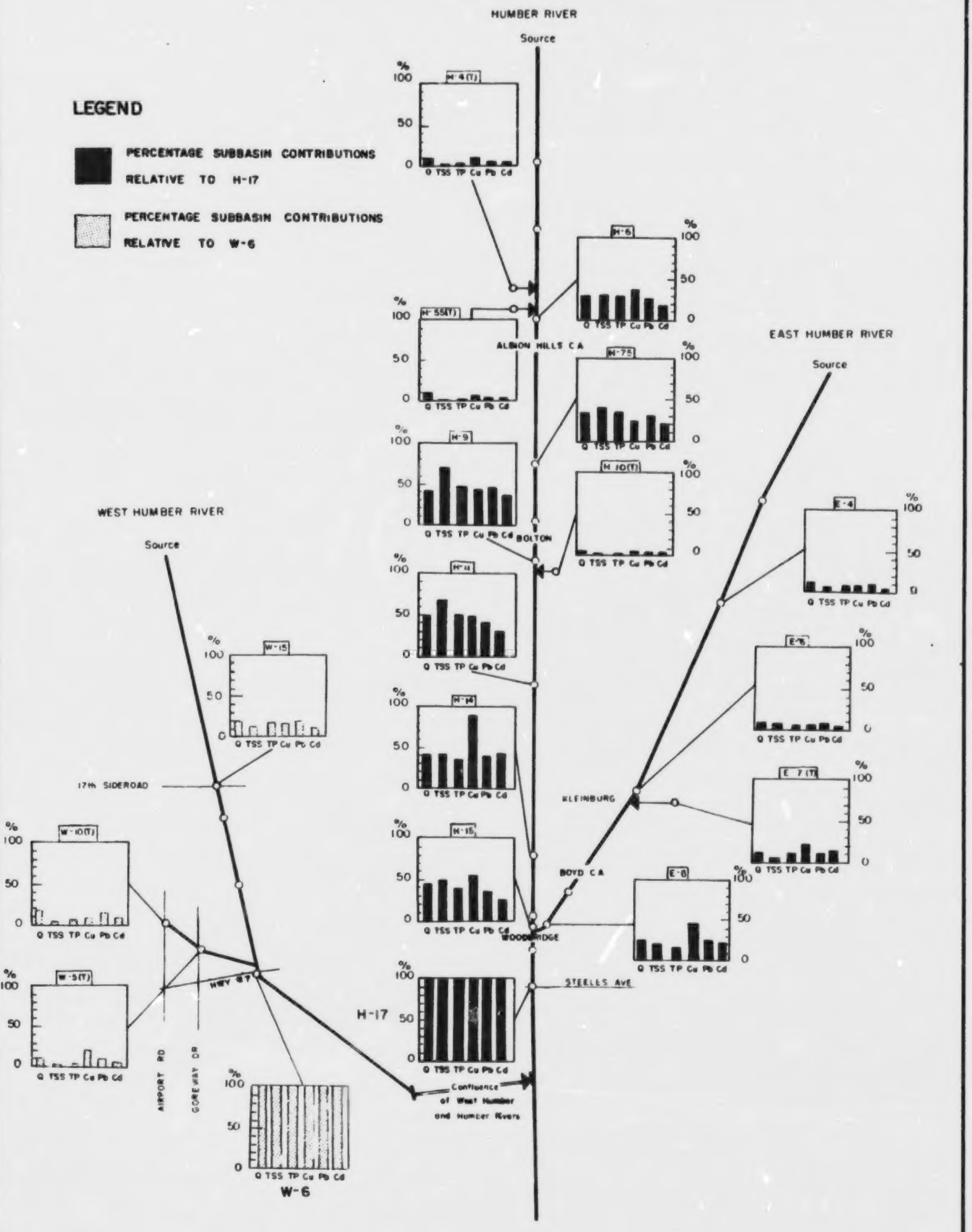
FIGURE 6

MARCH 1985

km

Table 5: Loads and "Mean" Concentrations For Sampled Portion of Wet Event

Station	Cumulative Drainage Area (sq. km)	Water Volume (x1000 cu.m.)	TSS Loading (kg)	TSS Conc. (mg/l)	TP Loading (kg)	TP Conc. (mg/l)	Cu Loading (kg)	Cu Conc. (mg/l)	Pb Loading (kg)	Pb Conc. (mg/l)
H-17	540	1872	266379	142.30	436	0.233	18	0.010	59.2	0.032
H-15	290	856	133961	156.50	169	0.197	10.2	0.012	21.8	0.025
H-14	281	770	107135	139.14	157	0.204	16	0.021	22.1	0.029
H-11	268	924	182183	197.17	226	0.245	8.79	0.010	27.3	0.030
H-10(T)	63	99.6	3805	38.20	6.85	0.069	1.56	0.016	2.74	0.028
H-9	188	790	185143	234.36	208	0.263	7.76	0.010	27.7	0.035
H-75	177	688	114160	165.93	150	0.218	4.4	0.006	18.1	0.026
H-6	146	514	87513	170.26	126	0.245	6.52	0.013	16.5	0.032
H-55(T)	44	178	1488	8.36	6.36	0.036	1.35	0.008	3.33	0.019
H-4(T)	23	167	7789	46.64	13.7	0.082	2.18	0.013	3.93	0.024
E-8	194	490	59469	121.37	76.7	0.157	8.76	0.018	14.2	0.029
E-7(T)	35	215	37551	174.66	49.8	0.232	4.3	0.020	6.62	0.031
E-6	141	189	24922	131.86	31.3	0.166	1.32	0.007	5.24	0.028
E-4	95	211	15925	75.47	29.1	0.138	1.3	0.006	5.32	0.025
W-6	143	622	84545	135.92	195	0.314	6.87	0.011	19.4	0.031
W-5(T)	59	67.3	2618	38.90	13.2	0.196	1.49	0.022	1.66	0.025
W-10(T)	21	115	3407	29.63	12.9	0.112	0.73	0.006	2.77	0.024
W-15	32	136	13211	97.14	36.1	0.265	1.2	0.009	3.73	0.027



the metropolitan toronto and region conservation authority

MINISTRY OF THE ENVIRONMENT

TORONTO AREA WATERSHED MANAGEMENT STUDY 85

UPPER HUMBER RIVER STUDY

CHEMICAL LOADINGS BY SUBBASIN
WET EVENT

FIGURE 7

MARCH 1985

2 1 0 1 2 km

H-10(T), which were consistently low. In no dry event did the loadings from any of these subbasins exceed 20% of the loading at H-17. Unlike TSS, TP loadings from subbasin H-6 corresponded closely to stream discharge, approaching 50% of the TP loading at H-17 during Dry Events 1 and 3. Loadings were slightly lower during the second event. Under all dry event conditions, the TP loadings increased between stations H-75 and H-9 (i.e. through the town of Bolton). During each event, the relative loadings increased about 30%; from 35 to 65% of the loading at Steeles Avenue during Dry Events 1 and 2 and from 107 to 144% during Dry Event 3. These loading increases are likely due to the Bolton STP discharge.

During dry weather conditions, relative TP contributions from subbasins through the central and southern portions of the Humber River (i.e. H-11, H-14 and H-15) ranged from 75 to 195% of the levels at H-17. The latter contribution occurred from the H-14 subbasin during Dry Event 3. Comparatively speaking, total phosphorus loadings from these subbasins generally exceeded corresponding stream discharges relative to values at H-17.

Total phosphorus inputs from the East Humber River subbasins were comparatively small relative to the loadings at Steeles Avenue. The most significant contribution occurred from the E-8 subbasin during Dry Event 1, when the TP loading was about 30% of the value at H-17.

Dry weather TP contributions from subbasins on the West Humber River were generally small relative to the loading at W-6. An exception occurred from the W-10(T) subbasin during Dry Event 3, when TP loading was equal to the loading at W-6.

Certain loading trends noted during the Dry Events were also seen during wet weather conditions. For example, the relative TP contributions from the tributary subbasins H-4(T), H-55(T) and

H-10(T) were also minimal during wet weather sampling. Similarly, increases in the relative TP loadings through the town of Bolton were observed during both the wet portion of Dry Event 2 and the Wet Event, although they were not as dramatic as those which occurred during the dry events. Differences in TP loadings from the H-11, H-14 and H-15 subbasins were apparent between the two wet weather sampling periods. Relative to H-17, the more significant contributions from these subbasins occurred during the wet portion of Dry Event 2.

Typically, wet weather TP loadings were relatively small from the East Humber River subbasins. Subbasin contributions were generally less than 10% of the value at H-17, increasing to about 20% at station E-8, near Woodbridge. Relative to station H-17, the discharge contribution from most East Humber River subbasins exceeded the corresponding TP contribution.

On the West Humber River during the wet portion of Dry Event 2, the most significant TP contributions occurred from the W-10(T) and W-5(T) subbasins, with respective loadings of 40 and 50%, relative to the value at W-6. During the Wet Event, relative TP contributions from these subbasins were much smaller.

Copper

In Dry Events 1 and 2, Cu loadings at H-6, the chemical sampling station closest to the source on the Humber River, had already reached the levels of the Humber River at Steeles Avenue. Although this was not the case in Dry Event 3, high loadings were found at the next station downstream, station H-75. The relative Cu contributions of the tributaries H-4(T), H-55(T), and H-10(T) in the three dry events were generally equal to their relative discharge contributions. The same was the case for most of the East Humber River, however, in the E-8 subbasin, relative Cu loadings tended to exceed relative discharges suggesting that subbasin E-8 could be a Cu source.

On the West Humber River, contributions of subbasin W-15 were minimal. Subbasins W-5(T) and especially W-10(T) had relatively high Cu contributions in Dry Event 2.

In wet weather, the relative Cu contributions from the upper portions of the Humber River were not as high as they had been in dry weather. In the wet portion of Dry Event 2, Cu loadings did not reach the level of Steeles Avenue until subbasin H-11. In the Wet Event, this occurred even further downstream, in subbasin H-14, however, relative loadings then decreased in subbasin H-15. Subbasin E-7(T) had a high Cu contribution in wet weather relative to its discharge. Wet Event Cu loadings at station E-8 reached nearly 50% of the Cu loading at station H-17.

There were high Cu contributions from subbasins W-5(T) and W-10(T) during the wet portion of Dry Event 2, however, this was not the case in the Wet Event. In the Wet Event, the bulk of the West Humber River's Cu load came from subbasin W-6.

Lead

The relative Pb contributions from subbasins throughout the study area were very similar during Dry Events 1 and 2. From almost every subbasin the loadings closely paralleled stream discharge, possibly suggesting inputs were generally of a diffuse nature.

Within the Humber River watershed, loadings from the tributaries H-4(T), H-55(T) and H-10(T) were minimal. Between stations H-6 in the Albion Hills and H-14 in the lower stretches loadings were typically between 60 and 85% of the loading at Steeles Avenue.

On the East Humber River, relative subbasin contributions were generally smaller due to lower stream discharges. An exception occurred from the E-8 subbasin near Woodbridge, where Pb loading was 40% of the value at H-17 during Dry Event 1 and 80% during Dry Event 2. This relative subbasin loading during Dry Event 2 is noteworthy because the corresponding stream discharge was only 40% and, thus, this is the only instance when Pb loading varied appreciably from discharge during either Dry Events 1 or 2.

On the West Humber River, the relative Pb contribution during Dry Events 1 and 2 was minimal from the W-15 subbasin. From subbasins W-10(T) and W-5(T), the respective loadings averaged 35 and 25% of the loading at W-6.

During Dry Event 3, all Pb levels in the Humber and East Humber Rivers were below the detection limit and, therefore, no relative parameter loadings could be determined for these rivers.

On the West Humber River, during Dry Event 3, the relative Pb loading was minimal from subbasin W-15. At W-10(T) the Pb concentration was below detection, despite a comparatively large proportion of stream discharge (80%), relative to W-6. Lead loading from subbasin W-5(T) was about 30% of the value at W-6.

As was the case with Cu loadings, relative Pb contributions from subbasins during wet weather conditions were generally not as high as had been noted during dry weather. This may suggest that dry weather sources of Pb become diluted during wet weather conditions. Relative Pb loadings during the wet portion of Dry Event 2 were similar to those occurring during dry weather conditions in that they generally corresponded to stream discharge. The exceptions occurred in the upper reaches of the Humber River, where the relative Pb contributions from subbasins H-6, H-75 and H-9 were only about 30% of the value at H-17, while the corresponding stream discharges were about 50%.

During the Wet Event, it appeared that a large proportion of the Pb loading was contributed by the H-17 subbasin itself. The relative Pb contribution at station H-15 on the Humber River was only 37% of the value at Steeles Avenue, and at station E-8 on the East Humber River, the relative loading was 24%. Stream discharges were correspondingly low suggesting that during severe storm events the relative contributions from the H-17 subbasin can be significant.

Relative to station W-6, the percentage contributions from the other subbasins on the West Humber River (W-15, W-10(T) and W-5(T)), were lower during the Wet Event than those recorded during Dry Events 1 and 2 (dry and wet portion).

Bed Sediment Chemistry

All but one of the 19 sediment samples collected from stations in the Upper Humber watershed were classified as very fine sand based on grain size analysis. Station W-5(T) was classified as medium to coarse sand. Silts and clays represented less than 3% by weight at all stations.

Cadmium concentrations were less than the detection limit (1.0 mg/kg) at all stations, and were therefore excluded from all subsequent analyses. Basic statistical analyses were performed on the remaining chemical data and the results are as follows:

	Mean	Minimum	Maximum
TP(mg/kg)	245	25 @ H-9	850 @ W-10(T)
Cu(mg/kg)	17	6 @ H-11, E-4	38 @ W-10(T)
Pb(mg/kg)	16	4 @ E-4	48 @ W-10(T)
Zn(mg/kg)	61	30 @ E-4	104 @ E-8

Stations were divided into two arbitrary groups; those with "low" concentrations and those with "high" concentrations as follows:

TP:	> 300 mg/kg	@	H-14, H-9, H-55(T), W-10(T), W-15
	< 100 mg/kg	@	H-17, H-11, E-6, E-4, W-6
Zn:	> 65 mg/kg	@	H-9, H-55(T), E-8, E-2, W-10(T)
	< 35 mg/kg	@	H-11, E-4, W-5(T)
Cu,Pb:	> 20 mg/kg	@	H-17, H-9(Pb only), E-8, E-2, W-10(T)
	< 10 mg/kg	@	H-11, H-75, H-9(Pb only), E-4

With only two exceptions, contaminant levels were not in exceedance of the MOE's open water disposal guidelines (MOE 1976a, 1978). Exceptions occurred at stations E-8 and E-2where the Zn concentration exceeded the guideline of 100 mg/kg.

Three groups of variables were positively correlated ($p<0.05$) as follows:

1) Zn, Pb, Cu, and silt.
2) Zn, TP, and LOI.
3) TP, and very fine sand.

In general, these correlations suggest that fluctuations in concentrations of metals and TP parallel fluctuations in the proportion of silt and very fine sand respectively. Also, comparatively high concentrations of Zn and TP are found in sediment of high organic content. Lead and Cu do not exhibit this positive association with organic content.

Land Use

Crop farming (Agriculture) forms the major proportion of land use within the Upper Humber study area. This land use presently comprises 69%, 81% and 87% of the Humber, East Humber and West Humber River basins respectively.

Within the Humber River watershed, pasture land (Pasture) tends to predominate in the more northerly subbasins (i.e. H-20, H-2, H-4(T), H-55(T) and H-6). This is likely because of the extremely hummocky terrain in this region which is better suited for livestock grazing than for crop farming. The shift from predominantly pasture land to agricultural land is dramatic as the Humber River exits the Oak Ridges Moraine and begins to flow over the more gently sloping till plain. From subbasin H-75 south to H-17 the agricultural component within each subbasin is typically between 45 to 75%. The proportion of Forested area within each subbasin is fairly consistent, averaging about 15%. The major Urban land use within the Humber River watershed is limited to subbasins encompassing Bolton and Woodbridge (i.e. H-8, H-9, H-19, H-15 and H-18).

Land use within the East Humber River basin parallels that of the Humber River although no significant pasture land was found. A fairly large urban component is present in the E-2 subbasin, due primarily to the communities of King City and Oak Ridges. The urban land use occurring within subbasin E-8 is associated with the town of Woodbridge.

Agricultural land use within the West Humber River basin is significant. It forms between 45 and 96% of the land use within each of the West Humber River subbasins. Grazing areas on the West Humber River typically border either one or both sides of the watercourse, and the field inventory, revealed many areas of extensive livestock access. The Urban and Forested components are minimal within most West Humber River subbasins.

Overland Sediment Delivery

Soil Loss Mapping indicated that the most significant overland delivery potential exists from subbasins in the central and northern portions of the Humber and East Humber River basins.

Overall, the H-10(T) subbasin (Cold Creek), has the potential to deliver the greatest amount of overland sediment, with 1,210 ha of targeted farmland (Appendix 5). Subbasins H-75 and H-11, situated above and below Bolton respectively, and the two upstream tributary subbasins H-4(T) ("Coffey Creek") and H-55(T) (Centreville Creek) all exhibit between 400 and 500 ha of targeted land.

On the East Humber River, the most significant subbasin is E-6 with a targeted area of 1,021 ha. The subbasins E-2, E-4 and the tributary subbasin, E-7(T) have 399, 554, and 430 ha of targeted land respectively.

The West Humber River basin exhibits considerably less overland sediment delivery potential than either of the Humber or East Humber River watersheds. The greatest potential exists in subbasins W-15, W-5(T) and W-6.

Considered in their entirety, the Humber River basin exhibits the greatest amount of targeted land with 4,203 ha targeted, followed by the East Humber River with 2,500 ha and the West Humber River with 863 ha (Appendix 5). If considered on a per unit area basis (ha of High overland sediment delivery potential/km^2), the Humber and East Humber River basins are quite similar exhibiting 12 and 13 ha/km^2 respectively. The West Humber watershed displays about 6 ha/km^2.

Field Inventory

Stream Bank Erosion

The total area of exposed erosive stream bank was calculated for each subbasin. These total erosive areas were then divided by the length of inventoried stream bank within the corresponding subbasin so that an estimate of the erosive area per unit length of stream bank (m^2/km) was obtained.

On the Humber River, subbasins H-19, H-14 and H-11 had the greatest per unit length stream bank erosion with values of 1,362, 961, and 624 m^2/km respectively. The increased TSS loadings observed within these subbasins in dry weather may be at least partially attributable to stream bank erosion. All other Humber River subbasins had erosive areas of less than 400 m^2/km, the lowest, 24 m^2/km, was in the uppermost subbasin, H-20. Erosive area was consistently high on the East Humber River, the highest (792 m^2/km) and lowest (384 m^2/km) values occurring within subbasins E-6 and E-2 respectively. Most of the West Humber subbasins had high erosion, although subbasin W-10(T) was low at 100 m^2/km.

Comparing the three rivers in their entirety, the West Humber River had the greatest erosive area per unit length at 1,486 m^2/km, followed by the East Humber at 1,281 m^2/km and the Humber at 949 m^2/km.

It should be emphasized that, while providing a comparative estimate of the degree of stream bank erosion within subbasins, the results are at best only an indicator of sediment loading potential. Soil type, stream discharge, land use, ground water movement and bank slope may substantially alter actual sediment loading from erosion.

Point Sources

Point source inflows were characterized as to whether they were natural (e.g. tributaries or springs) or anthropogenic (e.g. storm sewers, drainpipes, drainage ditches) and whether they were dry or flowing at the time of the inventory.

Anthropogenic inflows upstream of H-75 were primarily from pastoral, residential or small commercial land uses. The headwaters of Centreville Creek (H-55(T)) are in the community of Caledon East where some storm sewer outfalls exist.

Urban inputs were prevalent in subbasins H-9 and H-18 which corresponded to the towns of Bolton and Woodbridge respectively. These inputs were mainly storm sewers, some of which remained flowing in dry weather. Outfalls from sewage treatment plants (STPs) serving Bolton and Kleinburg were located in subbasins H-9 and H-19 respectively.

Anthropogenic inputs in subbasin E-8 corresponded to that area of Woodbridge located within the East Humber River drainage. A large number of anthropogenic inflows were also found on the East Humber River in subbasins E-2 and E-4. Subbasin E-2 included the communities of King City and Oak Ridges. Subbasin E-4 had a mixture of agricultural and commercial land, with most development concentrated along the Highway 400 corridor.

Anthropogenic inflows in the West Humber system were mostly agricultural in nature.

Livestock Access

For each subbasin, the percentage of watercourse length which was subject to livestock access was calculated from field inventories.

On the Humber River, the greatest amounts of livestock access were found in the more southerly subbasins H-19 and H-11 where, respectively, 66% (3.9 km) and 19% (2.0 km) of the river was subject to livestock access. Livestock access may be a contributing factor to the pronounced stream bank erosion problems in these subbasins. Also, TSS and TP loadings generally increased within these subbasins. Similar bank erosion problems and loading increases in the adjacent subbasin H-14 cannot be attributed to livestock access, however, as none was found.

On the East Humber River, livestock access was noted only in subbasins upstream of Kleinburg. Access was most prevalent in subbasin E-4 where 27% (2.8 km) of the river was affected.

As noted in the Land Use section, livestock pasturing in the West Humber watershed is significant because of its concentration along the watercourses. Field investigations showed that all subbasins were influenced by livestock: percentage access varied from 7% in subbasin W-2 to 73% in subbasin W-5(T). The extremely high FC counts detected throughout the West Humber watershed in wet weather may be partially attributable to runoff from livestock operations located in close proximity to the watercourses.

The generally low FC levels throughout the Upper Humber watershed in Dry Event 3 may relate in part to seasonal variation in pasturing and other farming practices. In contrast to field observations made in the summer and early fall, livestock would not be pastured in December.

4.0 Discussion

Microbiological sampling indicated widespread water quality degradation throughout the Upper Humber watershed. With the exception of Dry Event 3 when levels were somewhat reduced, FC counts regularly exceeded the PWQO at most sampling stations. Exceedances were most pronounced during wet weather. Generally, wet weather FC exceedances on the West Humber and East Humber Rivers were greater than those on the Humber River.

Fecal pollution in the Upper Humber watershed originates from a combination of rural and urban sources. FC:FS ratios in Dry Event 3 upstream of Bolton and Dry Event 1 on Centreville Creek suggest potential livestock fecal pollution. Animal fecal pollution was also indicated in the East Humber upstream of Woodbridge. Even in the relatively undeveloped upper reaches of the watershed FC exceedances were commonplace. For example, at station H-20, near the source of the Humber River, the geometric mean FC density was 112 counts per 100 ml in dry weather. At station H-2, further downstream, the dry weather geometric mean FC density was 1,106 counts per 100 ml. Field investigations indicated that the high FC levels at H-20 were likely the result of a problem in the immediate vicinity of the sampling station. Dry Event 3 FC:FS ratios indicated potential human sources in this area, while Dry Event 2 data suggest animal sources. This points out that, although an area may be largely undeveloped, significant local problems may still exist.

The towns of Bolton and Woodbridge provide good examples of the effects of local urbanization in the watershed. Within both communities there were numerous point sources, some of which were shown to be potentially significant dry weather sources of fecal pollution. Fecal coliform counts regularly increased through the towns and PA counts were generally high downstream of Bolton. High PA counts, which occurred in the upper reaches of the East Humber also indicate human fecal sources.

During the Synoptic Survey and Dry Event sampling the frequency and degree of TSS and TP exceedances were greatest in the Humber River subbasins between Bolton and Woodbridge. As well, these same subbasins (i.e. H-11, H-14, H-15) contributed the greatest dry weather loadings of TSS. These subbasins likewise had significant loadings of TP, however, large increases in TP loading also occurred upstream within the town of Bolton (i.e. subbasin H-9). Total suspended solids and TP increases between

Bolton and Woodbridge may relate in part to the observed stream bank erosion and livestock access problems in this area. Wet weather TSS and TP exceedances were more widespread. Mean exceedance ratios were higher in wet than in dry weather. The Bolton STP is a probable source of TP and TSS in this area.

In contrast to trends noted for TSS and TP, few significant spatial or weather-related differences in Cu or Pb concentrations were observed. These results corroborate other studies which indicate that significant inputs of Cu and Pb to watercourses can occur from diffuse atmospheric sources (precipitation and dry fallout) (Demayo _et al_. 1980, Demayo and Taylor 1981). One possible exception to this was subbasin E-8 which may be a source of Cu and Pb. The bed sediment sample from station E-8 had comparatively high concentrations of Cu and Pb as well as the highest observed Zn concentration.

The topography of the southwestern portion of the study area differs noticeably from the remainder of the Upper Humber watershed. The typically low relief and impervious nature of the Peel clays which predominate in the West Humber River basin inhibit rainwater retention, and during intense or prolonged storm events the watershed is extremely "flashy". In contrast to the Humber and East Humber River basins which have substantial base-flow contributions throughout the summer months, the summer base-flow component of the West Humber River is generally minimal. During summer months, as the soil loses its moisture, many watercourses in the watershed become intermittent and rely on periodic storm events to initiate flow. The only appreciable ground water contribution in summer occurred within the W-10(T) subbasin ("Gore Creek"), where several flowing springs were noted during field investigations. As a result of these consistent ground water inputs, "Gore Creek" is exceptional in that it maintains a measurable discharge during dry weather.

The significance of the West Humber's unique drainage basin topography was apparent during event sampling. In summer dry weather, the West Humber River had greatly reduced or intermittent flow; "Gore Creek" contributed a significant portion of the system's discharge. Even following the short-lived, intense rainfall in the wet portion of Dry Event 2 discharge in the West Humber River remained rather low. However, in response to the prolonged rainfall of the Wet Event, flow in the West Humber River became torrential, with peak discharge rivalling that of the Humber River at Woodbridge. During the Wet Event, subbasin W-6 became the major discharge and contaminant contributor.

As with subbasin W-6, the H-17 subbasin took on greater importance in the Wet Event. During the Wet Event, discharge and chemical loadings of the Humber River increased approximately 30% through subbasin H-17. This subbasin exhibited no loading increases of this magnitude in any of the other events, including the wet portion of Dry Event 2. The reason for subbasin H-17's increased importance in the Wet Event stems from a major portion of this subbasin being drained by "Rainbow Creek", a tributary which is confluent with the Humber River just above Steeles Avenue. The "Rainbow Creek" drainage basin is topographically similar to the West Humber River and is also urbanized near its confluence with the Humber River.

Other subbasins are likewise influenced by urbanization. For example, in subbasin E-8, near the mouth of the East Humber River, quicker storm water runoff resulted in rapid rises in river levels during the Wet Event.

The great disparity between dry and wet weather outputs of the West Humber drainage basin becomes significant when attempting to assess the relative impacts of the West Humber, Humber and East Humber Rivers on the lower Humber. Although the effects of

Claireville Reservoir are not fully known, it is apparent that the relative impact of the West Humber River on the Lower Humber would be greater under wet as opposed to dry conditions.

The decreased chemical and microbiological concentrations in Dry Event 3 may indicate that the importance of contaminant sources varies with season. The late fall and winter months are characterized by reduced or absent livestock pasturing, crop tillage and construction, frozen soils and stream banks less susceptible to wind and water erosion, and precipitation which is stored on the land as snow until spring. All of these would combine to reduce contaminant inputs to watercourses during this season.

Seasonal factors must also be considered in evaluating the Soil Loss Mapping. This mapping is designed to provide an indication of the relative potential of overland sources to deliver sediment to watercourses on an annual basis. The results of the mapping for the Upper Humber study area were not substantiated by wet weather sampling, however, this discrepancy is not surprising for several reasons. Of most significance is the fact that, on an annual basis, some 80 to 90% of overland sediment inputs typically occur during a critical 4 to 6 week period in the spring (D. Coleman, G. Wall, personal communication). By failing to adequately sample this period of the year, the relative importance of targeted lands (i.e. areas with a High overland delivery potential) appears to be considerably reduced.

Bed Sediment sampling did not appear to be a good indicator of subbasin chemical contributions, perhaps because samples were coarse.

5.0 Conclusions and Recommendations

Conclusions

1. Exceedances of PWQO (or other environmental standards) for FC, TSS, TP, Cu, Pb and Cd occurred under wet and dry conditions throughout the Upper Humber watershed. The magnitude and frequency of exceedance varied with season, with wet versus dry conditions, with characteristics of the storm events and with seasonal changes in land use activities. Sampling results under dry conditions in December (Dry Event 3) indicated lowest pollutant concentrations and loadings. No PWQO exceedances of Zn occurred in the Synoptic Survey, but Zn bed sediment levels on the East Humber at Woodbridge (E-8) and downstream of King City - Oak Ridges (E-2) exceeded Open Lake Disposal Guidelines (OLDG).

2. Fecal Coliform and TP concentrations showed similar trends throughout the watershed. Although the frequency of exceedance was high under both dry and wet conditions, the magnitude of exceedance was much greater in wet weather. Exceedances were particularly frequent in the lower parts of the watercourses, particularly in the Bolton-Woodbridge area. High PA counts in these areas suggest human fecal pollution. Sampling of point source inputs in this area suggests that urban sources may be partially responsible for these elevated FC and TP concentrations. Instream FC:FS ratios tend to support this conclusion. However, livestock access was extensive between Bolton and Woodbridge and this could also be contributing to higher parameter levels. River FC:FS ratios suggest animal fecal pollution occurred

upstream of Bolton on the Humber River, as well as on Centreville Creek and upstream of Woodbridge on the East Humber.

Extensive areas of livestock access occurred throughout the West Humber and on the East Humber east of Nobleton. The effects of livestock access in these areas may help to explain the FC and TP exceedances in the lower parts of these watercourses.

3. Total suspended solids concentrations in excess of 25 mg/l were rare in dry weather and generally occurred in downstream subbasins. Dry weather loading trends were similar in that they were greatest in the lower subbasins (i.e. south of Bolton H-11, H-14, H-15). Urban development and livestock access problems may be aggravating stream bank and channel erosion throughout these subbasins.

During the Wet Event, the main Humber and its tributaries north of Albion Hills made a relatively greater contribution to TSS loading at Steeles Avenue than during dry events. Tributary subbasins there (H-4(T), H-55(T)) had some of the largest areas of high overland sediment delivery potential. Large increases in Wet Event loadings also occurred through Bolton (H-9) and south of Woodbridge (H-17).

4. Copper concentrations usually exceeded PWQO throughout the watershed except during Dry Event 3. The frequency and magnitude of exceedances were similar in dry and wet conditions suggesting that Cu concentrations in surface waters during summer base-flow situations may be comparable to concentrations in storm event runoff from land surfaces. Diffuse atmospheric inputs are the most probable source.

5. Lead concentrations rarely exceeded PWQO during Dry Events 1 and 3, but during wet weather conditions, Pb concentrations increased slightly and exceedances were more common. However, in Dry Event 2 under low flow conditions widespread Pb exceedances occurred suggesting that the capacity of the watershed to dilute dry weather inputs was reduced. Diffuse atmospheric inputs are the most probable source.

6. Weather-related changes in subbasin flow contributions were significant. The West Humber River was intermittent along most of its length in summer dry conditions, yet discharge at Steeles Avenue during the Wet Event rivalled that of the main Humber at Steeles Avenue. This response may be partially explained by topography and soil type. The combination of poor soil permeability and low relief results in high stream discharges during storm events. Discharges in dry weather remain low because the base-flow component due to groundwater is minimal. Because of these discharge characteristics, the pollutant contribution of the West Humber River downstream of Steeles is likely important only during substantial runoff events. Its influence on the main Humber is unknown because all discharges and pollutant loads are mediated by Claireville Reservoir.

   During dry weather, the Humber River discharge at Albion Hills (27% of the drainage basin) represented over 50% of the discharge at Steeles Avenue. The East Humber discharge, at its confluence with the main Humber, represented 30 to 40% of the Humber River discharge at Steeles.

   During the Wet Event, discharge contributions changed dramatically. The main Humber between its confluence with the East Humber and Steeles Avenue (H-17) contributed 30% of the discharge at Steeles although it represents only 10.4% of the watershed area. Rainbow Creek, a tributary entering the Humber within this subbasin and urban areas of Woodbridge may be responsible for the increased discharge contribution. Discharge contributions from the Humber River north of Albion Hills and from the East Humber dropped to about 30% and 22% of total flow, respectively.

7. Tributaries were among the subbasins with the largest area of high overland sediment delivery potential (H-10 (T), H-4(T), H-55(T), E-7(T)). The Humber River near Bolton and the East Humber upstream of Kleinburg also had large areas of high overland sediment delivery potential. In total about 7500 ha of land were targeted comprising 12-13% of the Humber drainage area. Impacts of these areas were not apparent during the Wet Event, however, the greatest impact from these areas is probably during spring runoff.

8. Stream bank erosion was most extensive along the West Humber, the main Humber between Bolton and Woodbridge (H-11, HO-14, H-15) and the East Humber between Nobleton and Kleinburg (E-6). Impacts from small urban centres and livestock access may be aggravating bank erosion problems in these areas. The West Humber River had the greatest erosion area per unit length followed by the East Humber, then the main Humber.

Recommendations

1. Water quality problems in the Upper Humber watershed, although not of the magnitude of those occurring in the lower Humber, cannot be discounted in the development of

a water management strategy if PWQO are to be achieved. Note that the implementation of pollution control measures in the predominantly rural Upper Humber watershed and the achievement of at least local compliance with PWQO would be less costly than the initiation of control options for the lower Humber River.

2. It is recommended that the MTRCA coordinate an abatement program with MOE Central Region, the Ontario Ministry of Agriculture and Food, and municipalities beginning with fecal pollution point source inputs and those livestock access problems immediately upstream of the swimming areas in the Claireville and Boyd Conservation Areas. Other sources of fecal pollution in the upper Humber should also be addressed followed by point source inputs of trace metals and phosphorus.

3. More thorough evaluation of the behaviour of non-conservative parameters (i.e. FC, TP) should be conducted in the Upper Humber watershed to determine the potential effects of these parameters on the lower Humber River. This would involve obtaining information on the survival of bacteria and time of travel in the watercourses. A review of the microbiological data on the upper Humber should be undertaken in light of recent studies on use of different parameters as indicators of fecal pollution sources.

4. In view of the close association between TSS and contaminants, the role of sediment in pollutant transport should be further investigated. Where trace metals are of interest, sampling suspended as oppose to bed sediment may prove more beneficial.

5. The present and potential impacts of Claireville Reservoir on downstream quality should be evaluated.

6. Seasonal trends in contaminants loadings of the Upper Humber watershed should be further investigated, particularly spring runoff.

7. The relative importance of stream bank erosion and livestock access to instream water quality needs to be further evaluated, especially in the area between Bolton and Woodbridge.

8. A study should be conducted to assess the impacts of ongoing and future land use changes within the Upper Humber watershed.

9. Pathways (e.g. dry atmospheric fallout, precipitation, ground water) by which Cu and Pb enter the Upper Humber system should be further investigated.

10. The MTRCA should continue to apply the Soil Loss Mapping technique to other agricultural lands in its jurisdiction and verify and evaluate the results provided by this methodology.

6.0 Literature Cited

Baun, K. 1982. Alternative methods of estimating pollutant loads in flowing water. Wisconsin Dept. of Natural Resources. Technical Bulletin No. 133. 11 pp.

Coleman, D.E. 1982. Identification of priority management areas in the Avon River watershed. Stratford-Avon River Environmental Management Project. Technical Report R-4. 71 pp.

Demayo, A., M.C. Taylor and S.W. Reeder. 1980. Guidelines for surface water quality. Vol. 1 Inorganic chemical substances. Lead. Environment Canada, Inland Waters Directorate, Water Quality Branch. 36 pp.

Demayo, A., and M.C. Taylor. 1981. Guidelines for surface water quality. Vol. 1 Inorganic chemical substances. Copper. Environment Canada, Inland Waters Directorate, Water Quality Branch. 55 pp.

Geldreich, E.E., and B.A. Kenner. 1969. Concepts of fecal streptococci in stream pollution. J. Water Pollut. Contr. Fed. 41: R336-R352.

King, C.A.M. 1972. Beaches and coasts. 2 ed. Edward Arnold Ltd., London. 570 pp.

McNeely, R.N., V.P. Neimanis and L. Dwyer. 1979. Water Quality sourcebook. A guide to water quality parameters. Environment Canada, Inland Waters Directorate, Water Quality Branch. 89 pp.

MOE 1976a. Evaluating the impact of marine construction activities on water resources.

Bacteriological Water Quality Study Examining the Impact of Sediment and Survival Times in the Humber River and Black Creek

by

Patricia Seyfried and Elizabeth Harris
Department of Microbiology,
Faculty of Medicine,
University of Toronto.
Toronto, Ontario, M5S 1A8,
Canada

Abstract

Studies to assess the effect of sediment resuspension upon bacterial loading of the water column were carried out at six sites along the upper and lower Humber River and Black Creek. Bacterial contribution from sediment was measured during dry weather (before and after mechanical agitation of the sediment); wet weather; and intermediate periods within two days after a rainfall. The results showed that during dry weather, at locations with consistently high point source bacterial loadings, samples taken from the water column after mechanical sediment agitation exhibited higher fecal coliform and *Escherichia coli* counts than samples taken before agitation. During wet weather, bacterial densities were usually observed to be higher than those induced by dry weather sediment agitation. This suggests that localized sediment resuspension is only one of a number of sources of bacterial pollution during storm events.

The survival rates of water quality indicator bacteria were also monitored to determine their response to the Humber River environment. Bacterial survival was found to be somewhat

influenced by site-specific factors such as temperature and nutrient input. For example, *E. coli* exhibited a 80 to 98% die-off rate within 24 hours at sites impacted upon by sewers, while a greater than 99% die-off rate was noted at sites not receiving nutrient enriched effluents. *Streptococcus faecalis* exhibited die-off rates similar to *E. coli* at most of the sites, whereas *S. faecium* survived somewhat longer. All three indicators survived better when the water temperature was lower than 10°C. *Streptococcus bovis* was found to exhibit rapid die-off in surface waters, i.e. greater than 99% in 24 hours.

Introduction

The impact of fecal pollution upon surface water is dependent upon the type of input and the instream processes that may affect the downstream water quality. Two such processes which may contribute to downstream contamination from point and non-point pollution sources are bacterial transfer between the water column and sediment, and bacterial survival.

Although some bacteria remain free-floating in the aquatic environment, a large number become associated with solid particles (1). The mechanism of bacterial attachment to solid surfaces is by adsorption (2,3). By means of attraction forces, such as Van der Waal and chemical bonding, free-floating bacteria and bacteria-particle aggregates are continually removed from the water column to form part of the bed sediment (4).

Previous studies of the bacterial populations in sediments have shown that bacterial concentrations are considerably higher in the sediment than in the overlying water column (5-8). The bulk of bacteria in sediments reside in the surface layers where their activity is important to the mineralization of organic matter (9, 10). Fecal coliform and enteric pathogenic bacteria, such as Salmonella spp. have also been recovered from the upper two inches of the sediment bed (5, 11). Researchers have shown that higher recoveries of fecal coliform bacteria (100 to 1,000 fold increases over water column levels) may be obtained from sediments and have suggested that sediments may serve as a more concentrated and stable index of water quality (6).

Survival of fecal indicator bacteria in sediments is an important criterion in determining the extent to which they may be found in this environment. Extended survival and even multiplication of fecal coliforms in sediments have been shown to occur (7,8). Such phenomena may be due to the higher levels of organic carbon, ammonium, organic nitrogen and phosphorus found in sediment (12, 13).

Characteristics of the fecal indicator bacteria such as their ability to metabolize benthic nutrients (7, 8), withstand predatory pressure (14, 15), and metabolically compete with other microbes (8, 15) will dictate their survival time in sediments. The rate of sedimentation will also affect the recovery of these bacteria from sediment beds. Sedimentation rates will depend upon the adsorption capacity of both the sediment and the bacteria. Adsorbance is dictated most specifically by the surface chemistry of the microbe (16). The concentration of bacteria present at the water - solid interphase will also affect the extent of adsorption leading to possible saturation of the sediment surface (17). Inorganic particles in sediments are classified according to size into coarse sands (200 - 2000 um diameter), fine sands (20 - 200 um D.), silts (2 - 20 um D.) and clays (< 2 um D.). Clays can have a surface area in excess of 20,000 cm^2 g^{-1} and thus make the best adsorbents (4). Clays also have an added benefit in that they provide protection from radiation and predator - prey interactions (4).

Some environmental factors affect the rate of sedimentation because they affect the ability of the bacteria to adsorb to sediment particles. A pH >6 will interfere with adsorbance, while the presence of electrolytes and increased salinity will enhance floculation and sedimentation. Decreasing the salinity will cause desorption of bacteria from sediments (18).

Depth of the water column affects the rate of sedimentation; shallow systems may display an increased sedimentation rate. Sediment resuspension in shallow lakes and other surface waters may occur due to increased discharge rates, waves, and other wind induced turbulence, motor boats, swimming and wading (19). A number of reports have shown sediments to be reservoirs of enteric bacteria in densities sufficient to cause water quality deterioration and posr potential health hazards (20).

Streams and other watersheds represent a more dynamic system for studying the effects of sediment resuspension than lotic waters. Watersheds may be viewed as multiple storage and release systems (21) where water and sediment bacterial populations are in a constant state of interchange i.e. bacterial content in the water column is increased by fecal pollution input and sediment resuspension is reduced by sedimentation and die-off. Sediment resuspension and deposition are stream-flow dependent processes whereby increased flow facilitates the former and decreased flow the latter. How far bacteria are transported during high flow conditions depends upon the stream flow velocity. In a study by Matson et al (19) regression equations of the percent decrease in fecal indicator densities in water between two stations located 2.7 Km apart showed that minimal decrease occurred at high stream velocity (discharge). Since no additional inputs occurred along this portion of the river, the authors concluded that bacteria from upstream inputs were being transported downstream and that no sedimentation was occurring because of the high flow.

In general, water represents a more harsh environment for bacteria than sediments. The levels of available nutrients will be lower than those found in sediments and will vary depending upon the type of pollution input. Where nutrient levels are low, die-off may proceed more rapidly. Water with high dissolved organic carbon content, eg. impacted upon by sewage effluent, may permit extended survival or even support re-growth of heterotrophic bacteria (22). The presence of toxic materials, sunlight, and changes in water pH will affect the survivability of some types of bacteria (23, 24, 25). Temperature is also known to affect bacterial survival (26). Higher water temperatures will generally cause increased bacterial metabolism and thus an increased rate of decay while low temperatures tend to retard metabolism and permit extended survival by allowing the bacteria to exist in a dormant state. McFeters _et al_ (27) found that _E. coli_ survival response to temperature was inversely proportional between 5 to 15°C, but that above 15°C temperature became a less important factor in survival. Thermal stress can be beneficial to certain bacterial species depending upon their ambient growth temperatures. Regrowth of _Pseudononas aeruginosa_ in polluted waters at high temperatures can occur, especially when coupled with a high organic content. Some fecal coliform bacteria, eg. _Klebsiella_ sp., will also exhibit regrowth under these conditions.

This study was designed with the following objectives in mind: firstly, to determine the extent of bacterial exchange between sediments and the water column when sediments are resuspended and transported; secondly, to determine the survival time of various fecal indicator bacteria in the Humber River and Black Creek environment; thirdly, to provide the data required to help establish a method of inferring sources, eg. human versus non-human, by identifying the bacteria present at survey locations; and finally, to determine how sediments contribute to bacterial pollutant loading, analyze potential bacterial transport by sediments and the deposition capacity of different reaches of the river, relating effects to source type.

Methods

Sampling sites

Six locations were choosen in the upper and lower Humber River and Black Creek to provide study areas affected by different types of pollution.

The six study areas included:

1. Lower Humber River near Elhart Drive (priority storm sewer #254);
2. Black Creek near Hyde Avenue (combined sewer);
3. Lower Humber River at Emery Creek (receives industrial effluent);
4. Lower Humber River at James Gardens (with gull and geese roosting islands);
5. Upper West Humber River at Teston Road (cattle access area); and
6. Upper Humber River at Bolton (Bolton sewage treatment plant).

A geographical map of the locations is shown in Figure 1.

A total of four instream sampling points were chosen at each location in order to delineate the input source. These sites included:

1. 25 to 30 meters upstream from the source;
2. at source (immediately downstream of the pollution input);

3. 25 to 30 meters downstream; and
4. 50 to 60 meters downstream. Effluent samples from the sewer outfalls as well as samples from Emery Creek were also taken.

Only three of the six sampling sites, namely (1) Elhart Drive, (2) Black Creek, and (4) James Gardens will be discussed in this paper. The remainder of the data is included in a report submitted to the Ontario Ministry of the Environment.

Sampling Procedures

1. Dry weather

Sampling was conducted over a three day period and was preceeded by a minimum of two dry weather days. A sample, taken mid-point in the water column, was collected from the farthest downstream site in a study area. The river bottom at the site was raked with a garden rake until sediment resuspension was visible and then a second water sample was taken. This procedure was repeated at each site, moving in an upstream direction. The samples were labelled with respect to the site and study area and whether collection was prior to or after sediment agitation. Samples were chilled en route to the lab and analyzed within 24 hrs. after collection.

2. Wet Weather

Sampling was initiated at the beginning of a rain event, or within 24 hrs. after a rainfall, and was continued over a three day period. Rainfall antecedent periods (i.e. 24 to 48 hrs. after a rainfall) were considered to be inter-mediate weather conditions. The river bottom was not raked during storm events because the sediment resuspension was occurring naturally. Wet weather samples were collected and treated as described for dry weather samples.

Effluent samples from the sanitary and storm sewer outfalls were taken directly from the pipes. Samples from the combined sewer could only be taken when there was a flow during wet weather.

3. Survival Studies

In situ survival studies of fecal indicator bacteria were conducted at the six study areas in the summer and again in late October and mid-November to assess survival rates under different temperature conditions. Dialysis membrane filter chambers, with volume capacity of approximately 50 or 100 mL, were used to contain the pure cultures of *Escherichia coli*, *Klebsiella pneumoniae*, *Streptococcus faecalis*, *S. faecium*, or *S. bovis*. The inoculated chambers were transported to the sites in containers of iced Humber River water. Chambers were submerged and anchored to poles driven in the river bed at the source sampling site. Samples were taken from the chambers on three consecutive days by aseptically removing a small volume of culture and transporting it to the lab on ice. River temperatures were noted during the study.

Bacteriological Analyses

Samples were membrane filtered using Gelman GN6 47 mm cellulose nitrate filters with a pore size of 0.45 um.

To assess the number of fecal coliforms, the filters were placed on m-TEC agar and incubated at 44.5°C ± 0.5°C for 23 ± 1 hr. Filters with between 10 and 100 target colonies were then removed from the m-TEC plates and placed on filter pads soaked in a urea phenol red solution. A second count of all the urease negative E. coli colonies was then made.

Fecal streptococci were enumerated by planting the filters on m-Enterococcus agar (Difco) and incubating for 48 hrs. at 35°C.

Enterocci were recovered on m-ME agar which also contained indoxyl- -D-glucoside. The plates were incubated for 48 hrs. at 41.5 ± 0.5°C.

Pseudomonas aeruginosa densities were determined using m-PA agar with incubation at 41.5°C for 48 hrs. Data for the two aforementioned parameters are not discussed in this paper.

Analyses of the pure cultures from the survival studies were also performed by membrane filtration using m-TEC for E. coli and K. pneumoniae and m-ENT for the three species of fecal streptococci.

Sediment Size and Weight Analysis

Determination of the suspended sediment weights for both before and after agitation samples was performed by filtration of 100 mL of the sample onto pre-weighed Gelman filters. The filters plus sediment were dried overnight in a 37°C incubator and then weighed to obtain the weight of sediment per 100 mL of water.

Fractional sediment particle sizing was done by filtering 100 mL of the sample through pre-weighed poly-carbonate filters (nucleopore) of progressively smaller pore size. The filters ranging from 12 um to 0.2 um, were then dried and weighed to determine the weight of the various size fractions per 100 mL. Samples from selected sites were also submitted for particle size determination using electron microscopy.

Pollution Source Determination

Sources of pollution (i.e. human or non-human) were assessed by the biochemical identification of fecal streptococcal isolates obtained from upstream, source and downstream samples at each site.

Results and Discussion

The Effect of Sediment Resuspension on Water Quality during Different Weather Conditions

Dry Weather

The results showed that in some instances the effect of pollution input was only evident when the bed sediment was agitated (eg. Elhart Drive storm sewer outfall and James Gardens waterfowl access area, Figs. 2 to 7). High upstream levels may have obscured the pollution input; rapid deposition and dilution may also have had an effect. Dilution probably had the greatest influence due to the fact that these two locations are situated on the main Humber River and a comparatively large volume of water passes through each.

At the Black Creek combined sewer outfall (Figs. 8 to 10), a slight increase in the bacterial concentration was seen at the downstream 1 site before mechanical sediment agitation. This could have resulted from the small volume input during dry weather from the combined sewer outfall. Because the creek exhibits approximately 1/10 the flow of the main Humber River, even a small input would be noticeable. The fact that the increase was evident at the downstream site rather than at source was possibly due to the source site location, i.e. too far out in the stream to pick up the small effluent input. This input may not have dispersed through the creek until further downstream. Another factor could have been bacterial desorption from the sandy sediment below the input, since it has been shown that sandy sediments tend to adsorb bacteria more loosely (4).

The overall effect of mechanical sediment resuspension during dry weather was to increase bacterial concentrations in the water column, particularly at the Elhart Drive and James Gardens source sites (Figs. 2 to 7) and at the Black Creek downstream 1 site (Figs. 8 to 10). However, with the exception of the James Gardens source site, the concentrations achieved were not as high as during wet weather, suggesting that local sediment resuspension is only one of many contributing sources during wet weather events. At the James Gardens source site, where fecal coliform and E. coli concentrations were higher during dry weather after mechanical sediment resuspension, it is possible that the wet weather peak was missed since the flow is swift in this area (average wet weather flow = 4.468 cm^3/sec. In addition, the sediments at source are composed of very fine organic material which could have been transported downstream at the onset of the storm before sampling had commenced. It is also quite possible that the sediments at this site are so highly contaminated with bird feces that the wet weather contamination from upstream does not have the same impact as resuspension of sediment continuously contaminated with frest fecal material.

In instances where sediment resuspension brought about little change in the water column fecal indicator levels, such as E. coli levels at Black Creek, the type of pollution input may have been responsible. The combined sewer outfall at Black Creek is a weather dependent input and does not provide constant high level bacterial loadings. Under these conditions fecal indicators such as E. coli, that have a short survival time (i.e. greater than 90% decline in three days) (28), would not exhibit a buildup in the sediments during periods of dry weather. The somewhat greater increases in fecal coliform and fecal streptococcus levels after sediment agitation at the Black Creek upstream and downstream sites is probably due to older inputs since fecal coliforms, other than E. coli and fecal streptococci, tend to survive for longer periods in the environment (29).

Constant dry weather inputs from pollution sources such as the Elhart Drive storm sewer outfall, which exhibits dry weather effluent levels of 25,847 fecal coliforms and 17,692 E. coli per 100 mL, and the James Gardens waterfowl access area provide continuous bacterial loading to the sediment. This tends to offset ongoing bacterial die-off and sediment transprot and results in higher levels after sediment agitation in dry weather. However, the concentrations tend to decrease from sourec to downstream.

Mechanical sediment resuspension also increased levels of suspended sediments in the water column (Figs. 11, 12 and 13). The greatest effect was noticed at sites which had the lowest water column suspended sediment levels before sediment agitation. This would indicate that there is a higher rate of deposition occurring at these sites. James Gardens source site (Fig. 12) was an exception in that it exibited the highest levels of suspended sediments both before and after sediment resuspension. There may be sufficient ongoing inputs of fecal material at this siet to maintain high water column suspended sediment levels.

Intermediate Weather

During intermediate weather conditions (i.e. 24 to 48 hrs. after a rainfall event) the levels of both suspended sediments and fecal indicator bacteria in the water column fell somewhere between dry and wet weather concentrations. Once again it may be seen that the effect of the pollution inputs on the water column is not always evident prior to mechanical sediment resuspension. At Black Creek where the fecal indicator concentrations were lower than during dry weather, with the exception of fecal streptococci at source and downstream, it is possible that a flushing effect has occurred in the stream; the channel is quite narrow and the creek exhibits a rapid increase in flow during wet weather. The level of suspended sediment in the water column decreases from upstream to source as well and this may be the result of increased deposition as the stream flow decreases after wet weather Jenkins el al (21) also observed increased sedimentation in response to stream velocity decrease.

Mechanical sediment resuspension during intermediate weather caused increases in bacterial concentrations and suspended sediment levels, but again the increases at the Black Creek and Elhart Drive locations were not as high as those exhibited during wet weather. At James Gardens, the suspended sediment levels were higher during intermediate conditions in comparison with wet weather and, as previously indicated, this may be due to direct deposits of fecal material. The Elhart Drive bacterial concentrations measured post agitation during intermediate weather conditions were higher than the post agitation concentrations achieved in dry weather, possibly due to increased deposition after a rainfall. This was also true for the James Garden sites with the exception of the source site where the levels were slightly lower possibly because of washout of the freshly deposited fecal material during the higher wet weather flows. Lower levels at the Black Creek source and downstream sites, in comparison with dry weather post sediment agitation, may have been due to a washing and or scouring effect in the creek as a result of heavy rainfall.

Wet Weather

During wet weather, there were high levels of both fecal indicators and suspended sediments in the water column, but frequently the bacterial increase was proportionately greater than the suspended sediment increase. As during dry and intermediate weather conditions, the effect of the pollution inputs was somewhat obscured in the water column during wet weather due to high upstream contaminant levels and dilution. It is interesting to note that this obscuring effect occurs at Black Creek even though the combined sewer outfall exhibited concentrations of 1,500,000 fecal coliforms and 1,100,000 E. coli per 100 mL. The fecal coliform and E. coli levels from the Elhart Drive storm sewer effluent were lower due to dilution from storm runoff.

Fecal coliform to fecal streptococcus ratios tended to drop during wet weather even though there were fresh fecal inputs and higher fecal coliform and E. coli levels present. It is possible that streptococci from older or distant inputs are surviving in the sediments and are causing increases in the water column levels when sediments are agitated during storms. Additional streptococcal organisms from plant sources can also be washed into the river through storm runoff (30, 31). Other workers have suggested that the FC/FS ratio should be used with caution because of the differential die-off rates of the two indicators. Furthermore, the effect of environmental factors may alter their relationship and may least to erroneous interpretation of the ratios (11, 32, 33).

Survival of Indicator Bacteria During Different Seasonal Conditions

The length of survival of E. coli under summer weather conditions (i.e. water temperature = 18 to 25°C) (Figs. 14, 15 and 16) was very short. Generally there was a 97 to 99% die-off rate within 24 hrs. with an equivalent or slightly lower rate occurring over day two and day three. At Black Creek, E. coli exhibited a lower die-off rate (i.e 80.2% in 24 hrs.) which may be attributed to high nutrient loadings in the creek (average total Kjeldahl nitrogen loading to the lower Black Creek area is 16,494 g/day; average NH_3-N loading is about 9,305 g/day; and total phosphorus loading is approximately 2,394.4 g/day (33).

Streptococcus faecalis var liquefaciens tended to survive somewhat better during summer conditions except at the Elhart Drive location where it decline more rapidly than E. coli. Dutka and Kwan (34) also found the E. coli survival response to be much greater than S. faecalis in Lake Ontario waters. S. faecium exhibited a slower die-off rate than either S. faecalis or E. coli during the summer. This bacterium has been known to survive for more than 28 days in surface waters (29).

Under winter conditions (average water temperature = 6 to 9°C (Figs. 17, 18, and 19) the survival response of all three indicator bacteria increased. For E. coli, the initial 24 hr. percent die-off rate decreased at both the James Gardens and Black Creek sites and increased at the Elhart Drive site. However, during the second and third day the E. coli die-off rate decreased dramatically at the Elhart Drive and Black Creek locations. By day three, the die-off rate for *E. coli* had increased to 100% at the Black Creek site.

S. faecalis and *S. faecium* were found to have similar die-off rates during winter conditions. It has been suggested that *S. faecium* survives longer than *S. faecalis* in warmer polluted waters, but that both organisms assume closer rates of decline in colder or pristine waters (Dufour, personal communication, 1985). *S. bovis* exhibited a very rapid die-off rate (i.e. greater than 99% in 24 hrs.) during the winter. Similar rates have been reported for this bacterium under summer conditions (28). Unlike other members of the fecal streptococcus group that may be recovered from environmental sources, *S. bovis* is specific to the feces of certain warm blooded animals (35). Its rapid die-off indicates that a recovery of this organism from surface waters is indicative of recent animal fecal inputs.

Although *in situ* survival of other members of the coliform group (i.e. *Enterobacter* and *Klebsiella)* was not studied at the three locations, previous investigations have shown that these bacteria can persist in surface waters for longer periods than *E. coli* (29,36). The ability of these species to utilize internal endogenous reserves may aid in increasing their survivability in surface waters. The fact that some members of these above mentioned species are encapsulated may also enhance their survival (29).

Regrowth of coliforms in waters enriched by sewage, food processing plant and pulp and paper mill effluents has also been reported (37,38), as well as regrowth in sediments and soils (39,40). Since a differential die-off rate occurs among members of the coliform group, the proportion of E. coli in fecal coliform populations will decrease with time. Thus the E. coli to fecal coliform ration (EC/FC ratio) may be a good indication of the age of the contamination.

Summary

A comparison of the overall average increase in bacterial concentration and sediment weight during dry and intermediate weather conditions caused by sediment agitation at the three locations is presented in Table 1. The increase in water column bacterial concentrations from dry to wet weather as well as the percent die-off in 24 hrs. at each location is also given.

The greatest increases in both sediment, fecal coliform, and E. coli levels during dry and intermediate weather were obtained in the Humber River at James Gardens. It would thus appear that this location has the greatest potential for deposition under these weather conditions possibly because of the shallowness of the water column in this area. The high concentration of bacteria in the sediment is due to the continuous fecal input from waterfowl, with the possibility of further contributions from upstream loadings to this location. Although the die-off rate of E. coli was highest at this location (i.e. 99.96% in 24 hrs.), it is possibly off-set by the magnitude of the ongoing contaminant inputs.

At Elhart Drive the dry weather increases in recovery of fecal indicator bacteria were considerably lower than at James Gardens but higher than at Black Creek. The E. coli die-off rate was second highest at this location, again suggesting that continuous inputs of bacteria can off-set high die-off rates allowing far accumulation in the sediments under dry conditions. The decreased level of sediment bacterial accumulation in comparison with James Gardens is most likely due to factors such as lower upstream loadings, less sediment deposition, and the nature of the input at this location (i.e. storm sewer outfall as apposed to direct fecal input).

Combined sewer outfalls such as the Hyde Avenue outfall are a major source of bacterial contaminants to Black Creek during wet weather. The greatest increase in bacterial concentrations from dry to wet conditions was observed at this location with fecal coliforms and E. coli exibiting increases of 12,738 and 7,628 bacteria per 100 mL, respectively. The increased recoveries obtained after sediment agitation during intermediate weather are possibly related to high loadings during the preceeding storm event, and better survival of indicator bacteria in Black Creek.

During dry weather, the Black Creek location exibited the lowest sediment accumulation of bacteria. This probably due to minimal contaminant input during dry weather, a lower rate of sediment deposition, and the adsorption characteristics of the sandy sediments at this location. The problems associated with using relative proportions of fecal coliforms to fecal streptococci (i.e. FC/FS ratio) in stream becomes obvious when comparing the three locations. For example, there is little variation in the ratio during dry weather at the three locations. Furthermore, the highest ratio was obtained at James Gardens where the fecal input is known to be of non-human origin. During wet weather, as previously mentioned, the relative concentration of fecal coliforms to fecal streptococci decreases at all locations due to resuspension of older or distant inputs. The differential die-off rates of the two indicators would account for the survival of fecal streptococci in older inputs.

Conclusions

Bactreial exchange between the sediments and the water column does occur when sediments are resuspended; however, the extent to which this process occurs depends upon the survey location (i.e. type of pollution input), the sampling site at a given location (i.e. relative to the input), the flow rate of the river, prevailing weather conditions, and the bacterial parameter being analyzed.

The results of this study indicates that the greatest accumulation of contaminants in the sediment occurs at locations where sediment deposition is combined with continuous high level pollution input. The greatest local impact appears to be in areas receiving direct fecal deposits. However, the overall degradation of water quality in the Humber River watershed appears to be due to the cumulative effect of a large number of different sources; localized effects are not indicative of the impact of any one pollution type on the entire water course.

In determining the source of the pollution (i.e. human or non-human), it is necessary to develop an interpretive methodology combining information obtained from different types of data (eg. site observation, upstream inputs, bacterial concentrations and species). Reliance on one piece of information, such as the FC/FS ratio, is not sufficient. Interpretive tools such as EC/FC ratios however, may be useful in determining the age of a pollution input.

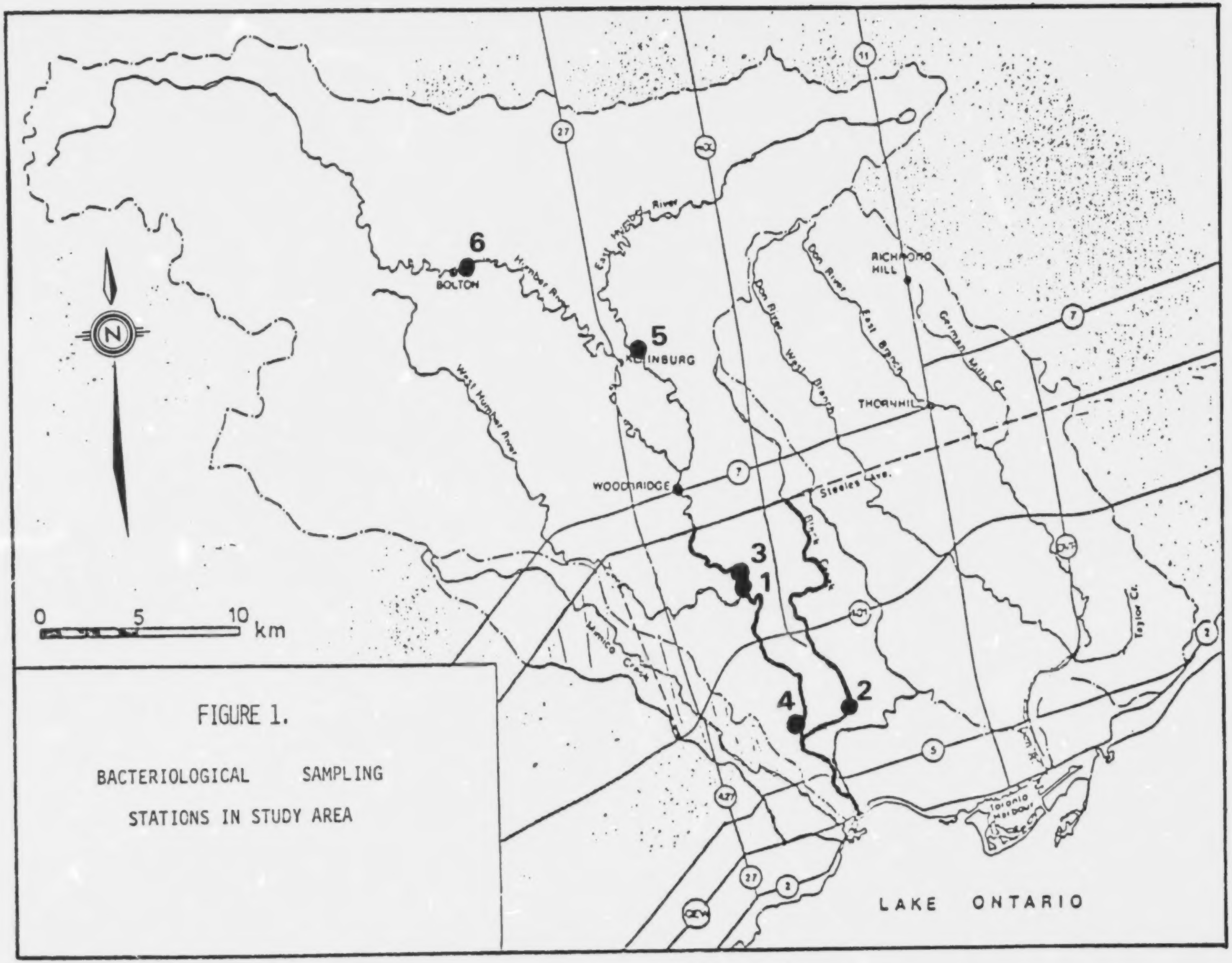


FIGURE 1.

BACTERIOLOGICAL SAMPLING STATIONS IN STUDY AREA

FIGURE 2 IMPACT OF ELHART DRIVE STORM SEWER ON IN STREAM FECAL COLIFORM CONCENTRATIONS

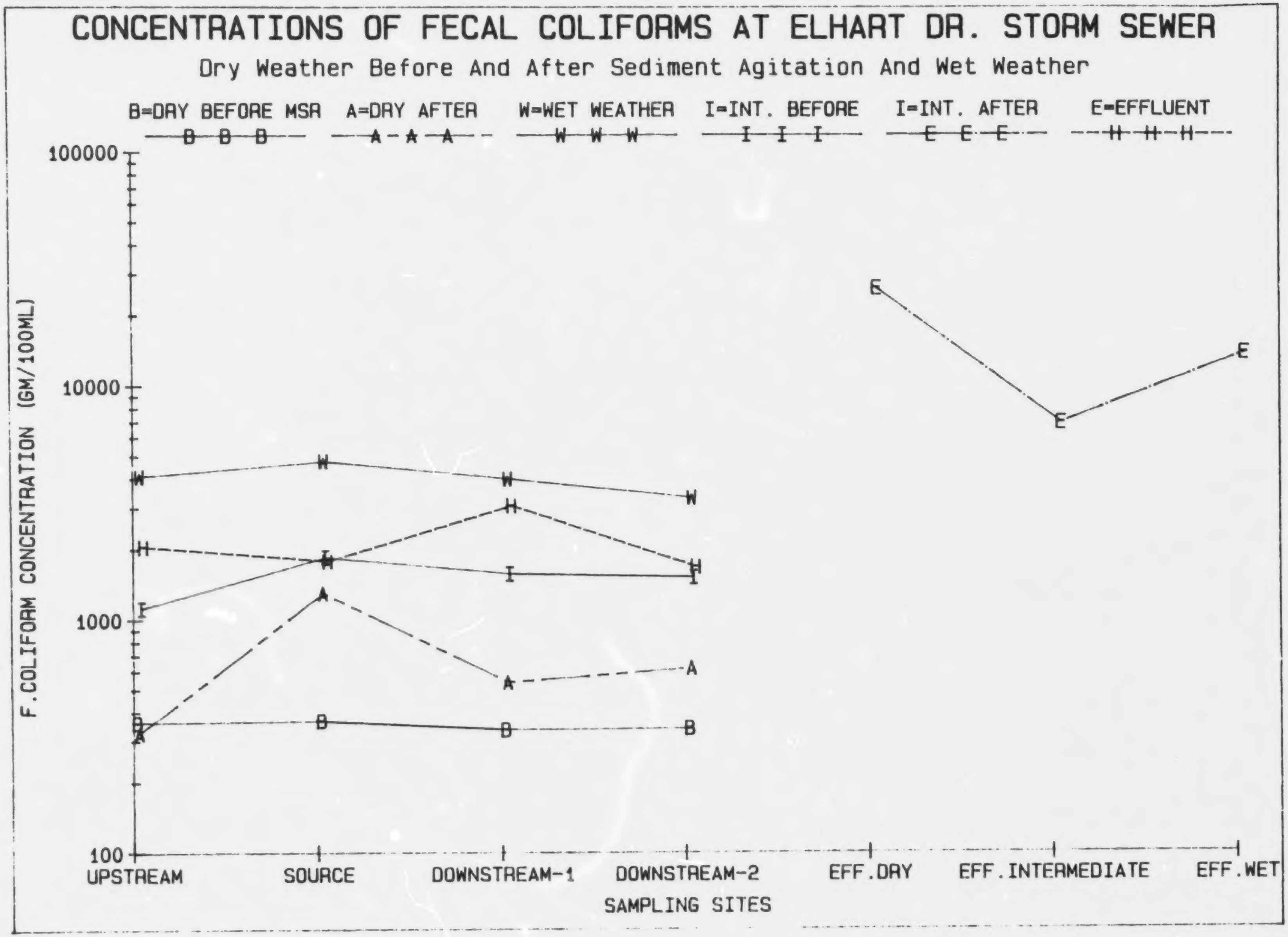


FIGURE 3: IMPACT OF ELHART DRIVE STORM SEWER ON IN STREAM E. COLI CONCENTRATIONS

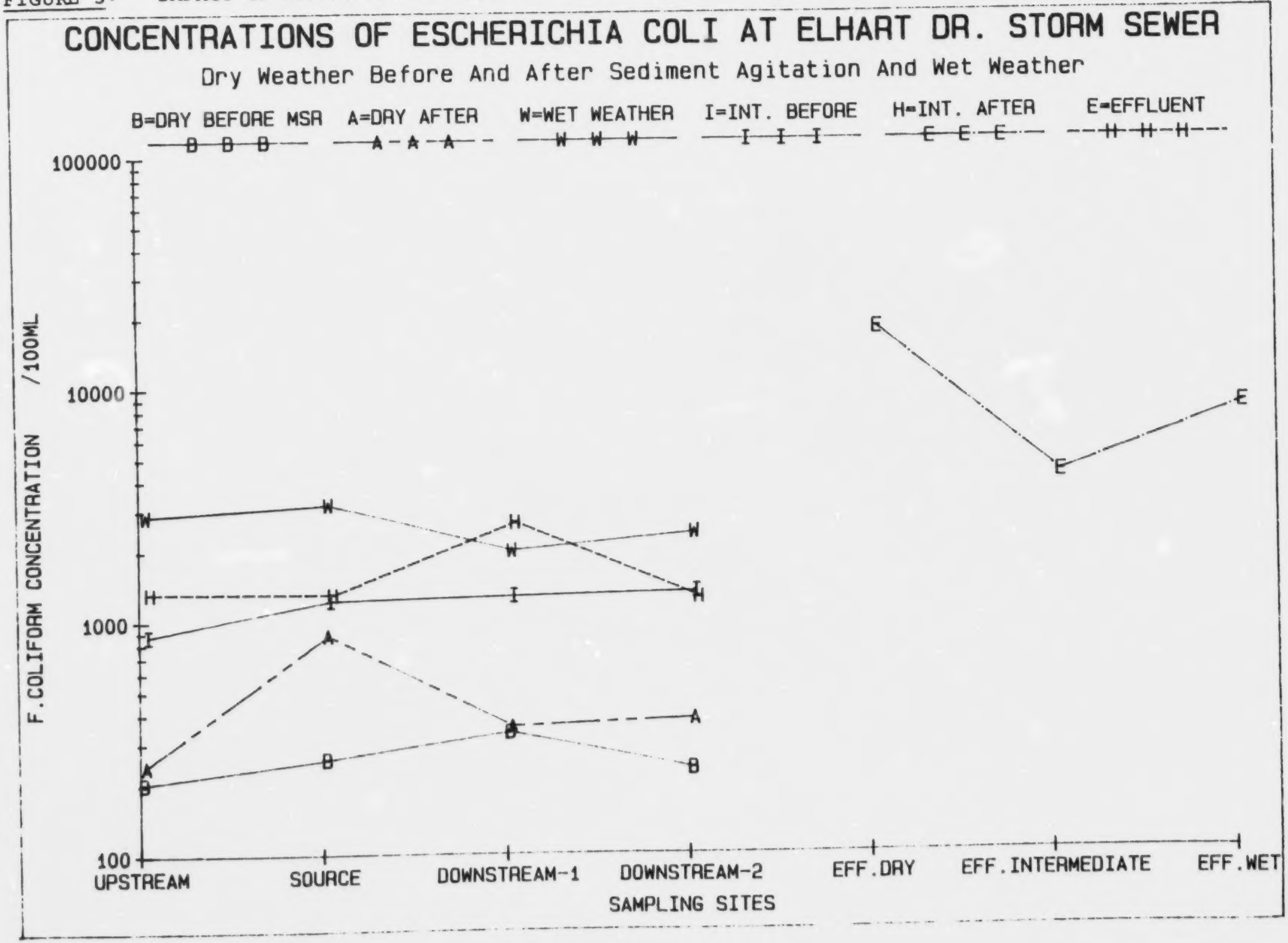


FIGURE 4: IMPACT OF ELHART DRIVE STORM SEWER ON FECAL STERPTOCOCCI CONCENTRATIONS

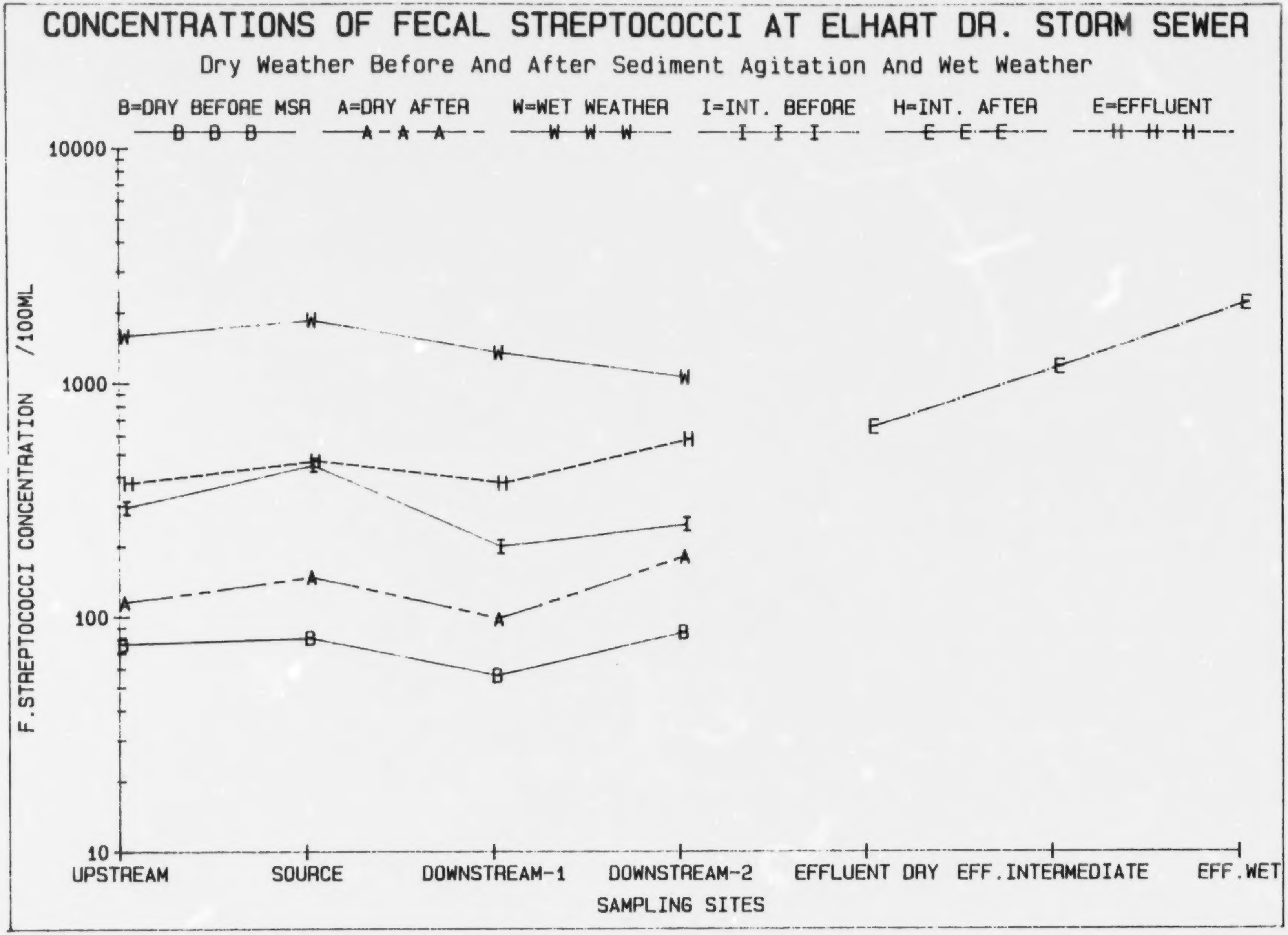


FIGURE 5: IN STREAM FECAL COLIFORM LEVELS AT JAMES GARDENS

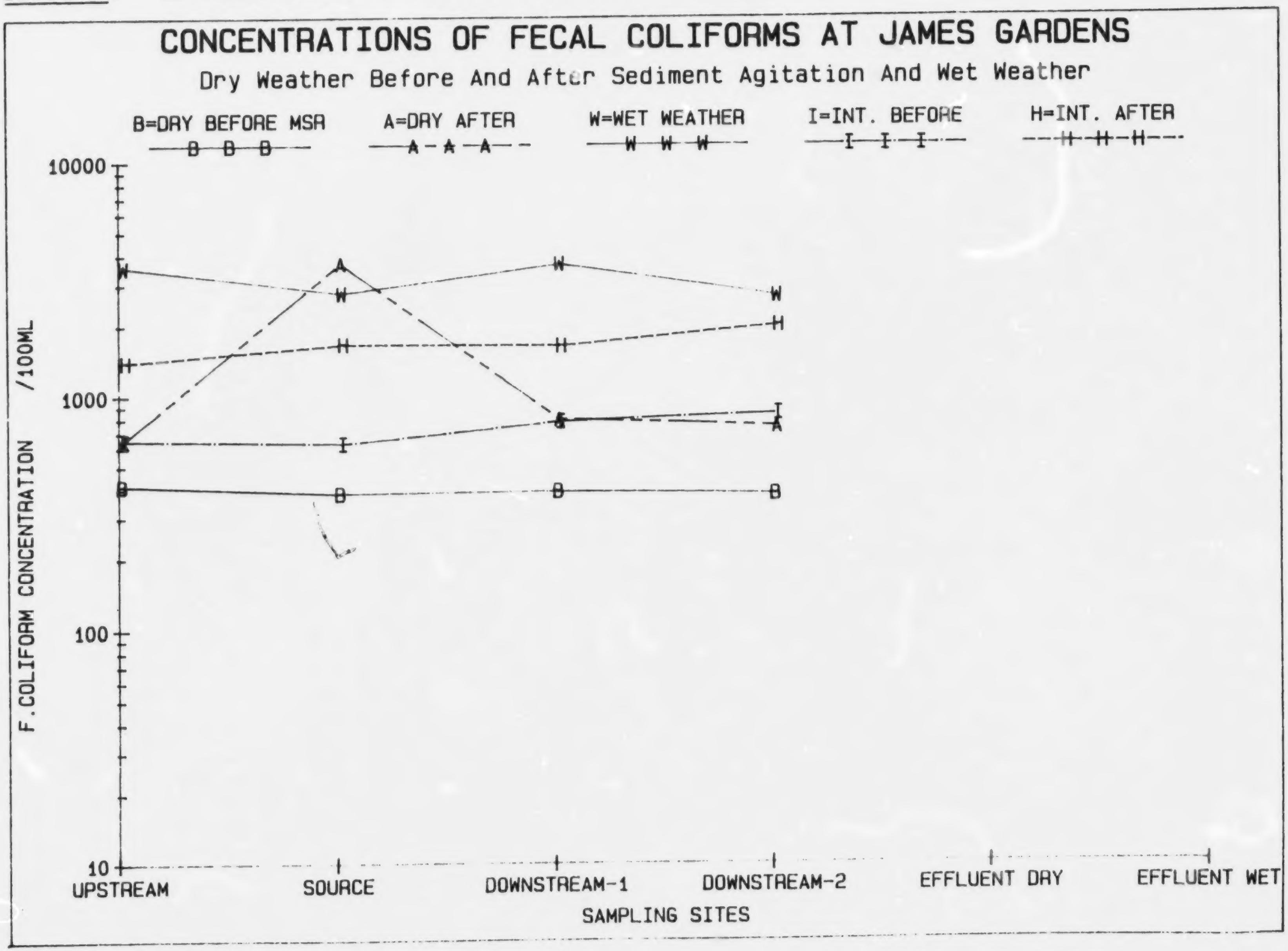


FIGURE 6: IN STREAM *E. COLI* CONCENTRATIONS AT JAMES GARDENS

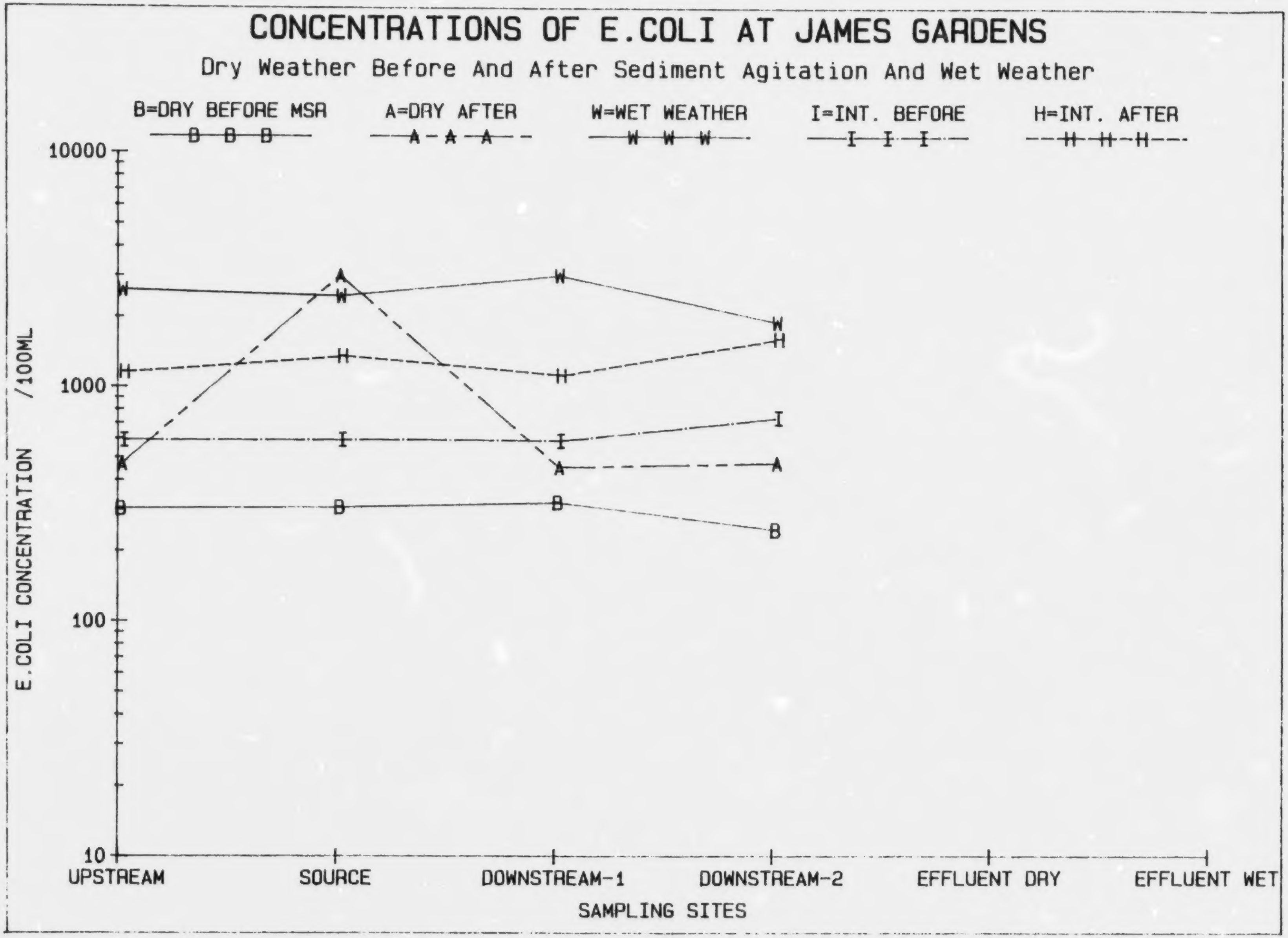


FIGURE 7: IN STREAM FECAL STREPTOCOCCI LEVELS AT JAMES GARDENS

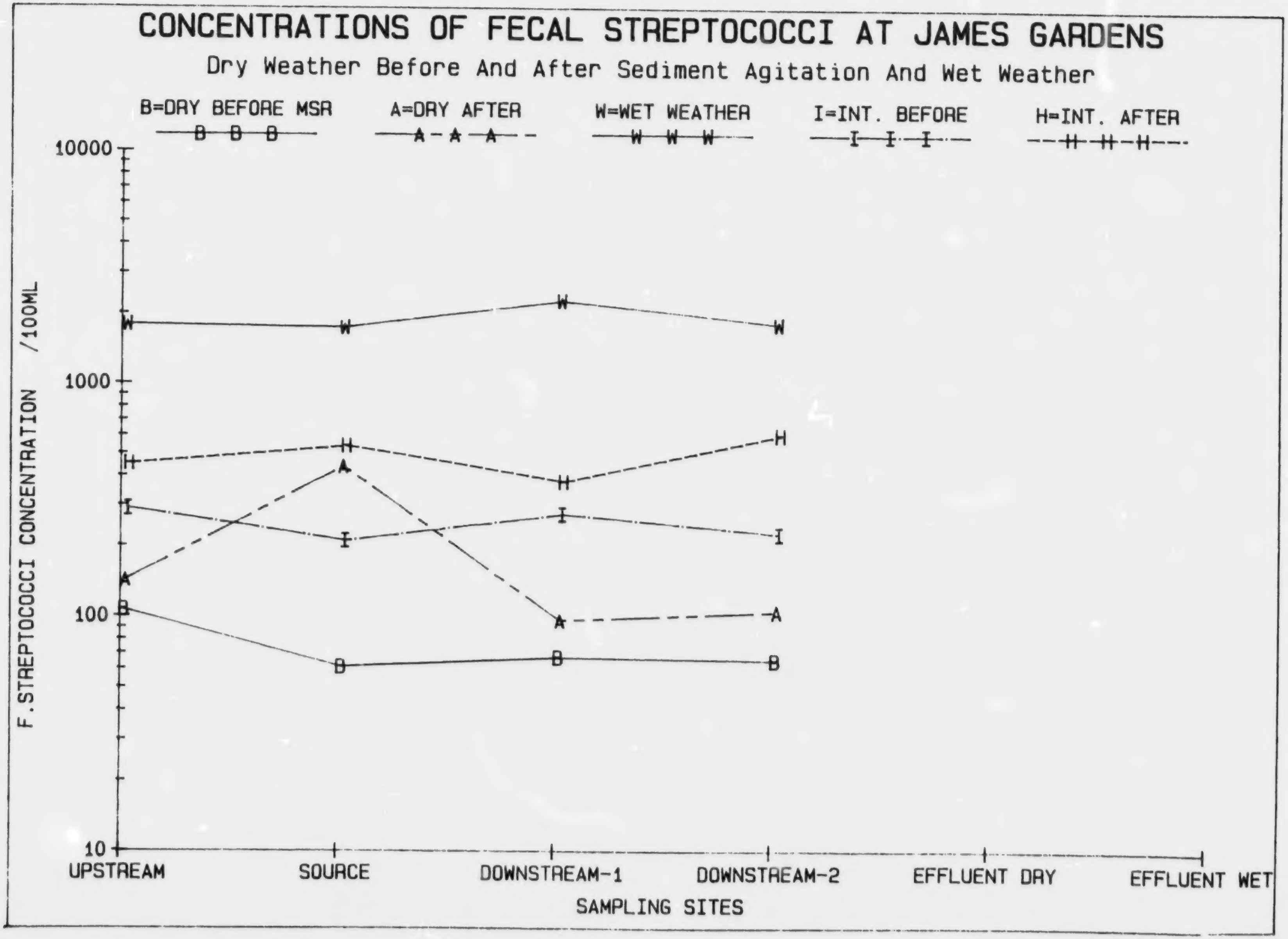


FIGURE 8: IMPACT OF BLACK CREEK COMBINED SEWER OUTFALL ON IN STREAM FECAL COLIFORM CONCENTRATIONS

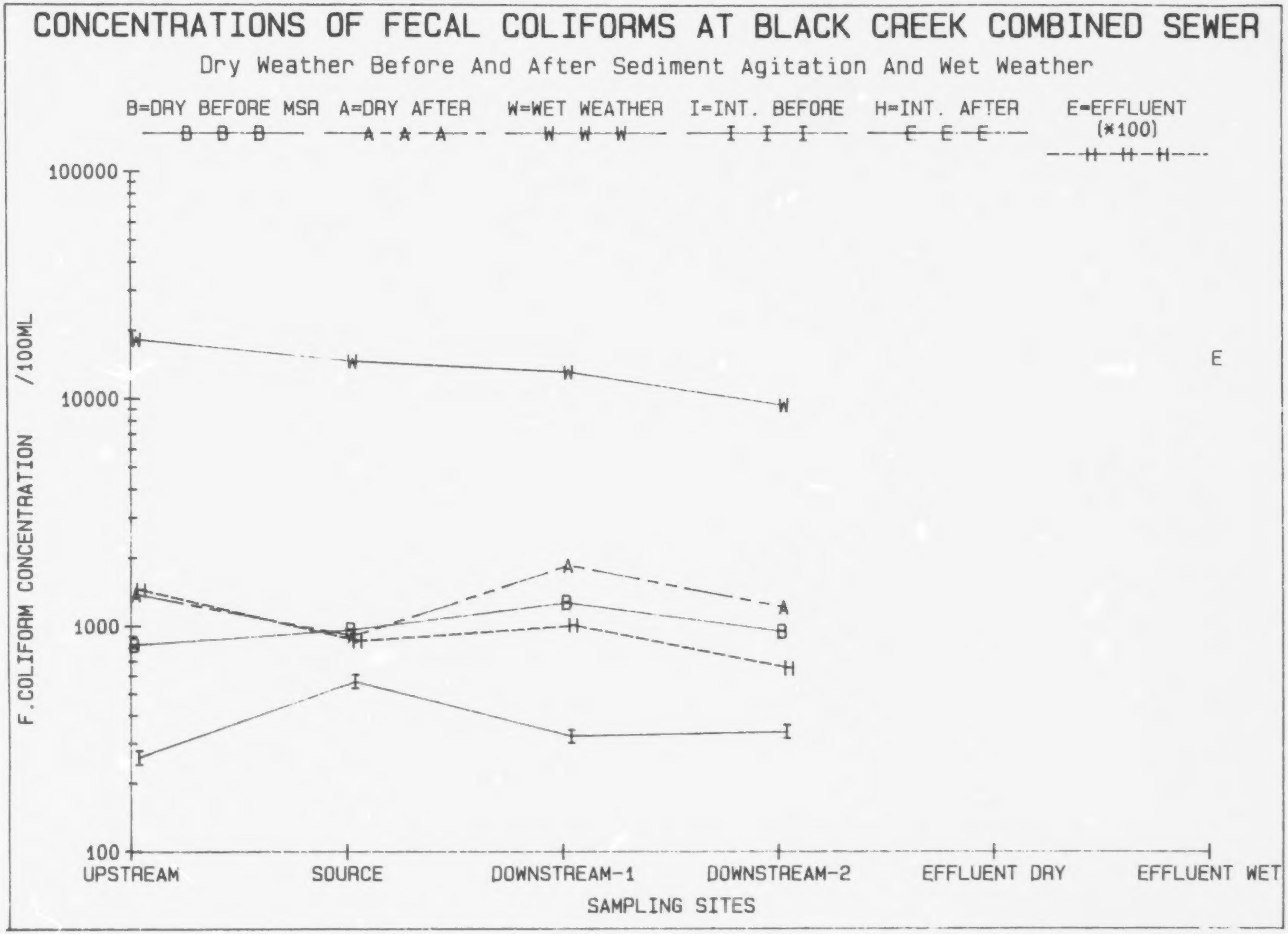


FIGURE 9: IMPACT OF BLACK CREEK COMBINED SEWER OUTFALL ON IN STREAM E. COLI CONCENTRATIONS

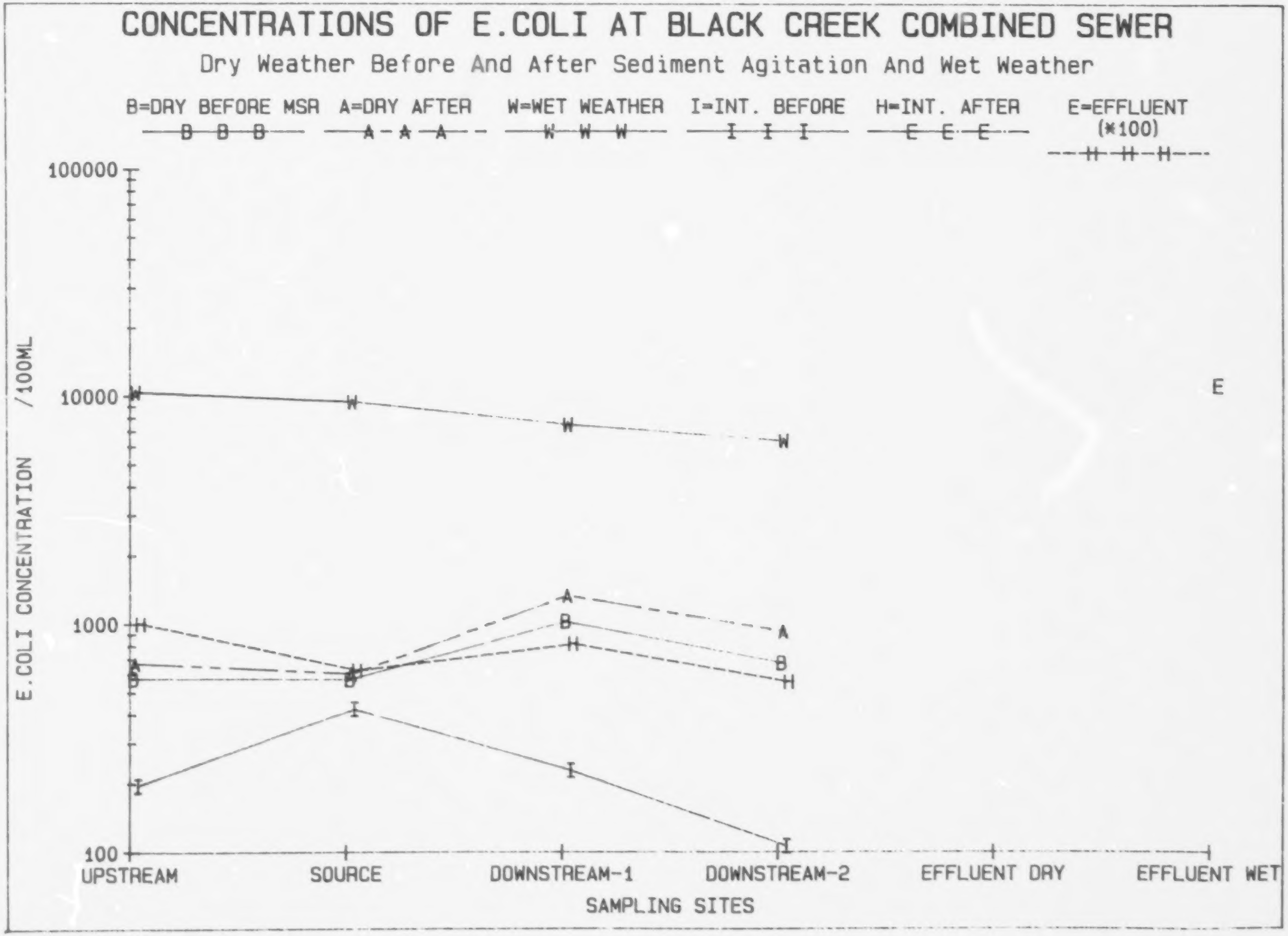


FIGURE 10: IMPACT OF BLACK CREEK COMBINED SEWER OUTFALL ON IN STREAM FECAL STERPTOCCI LEVELS

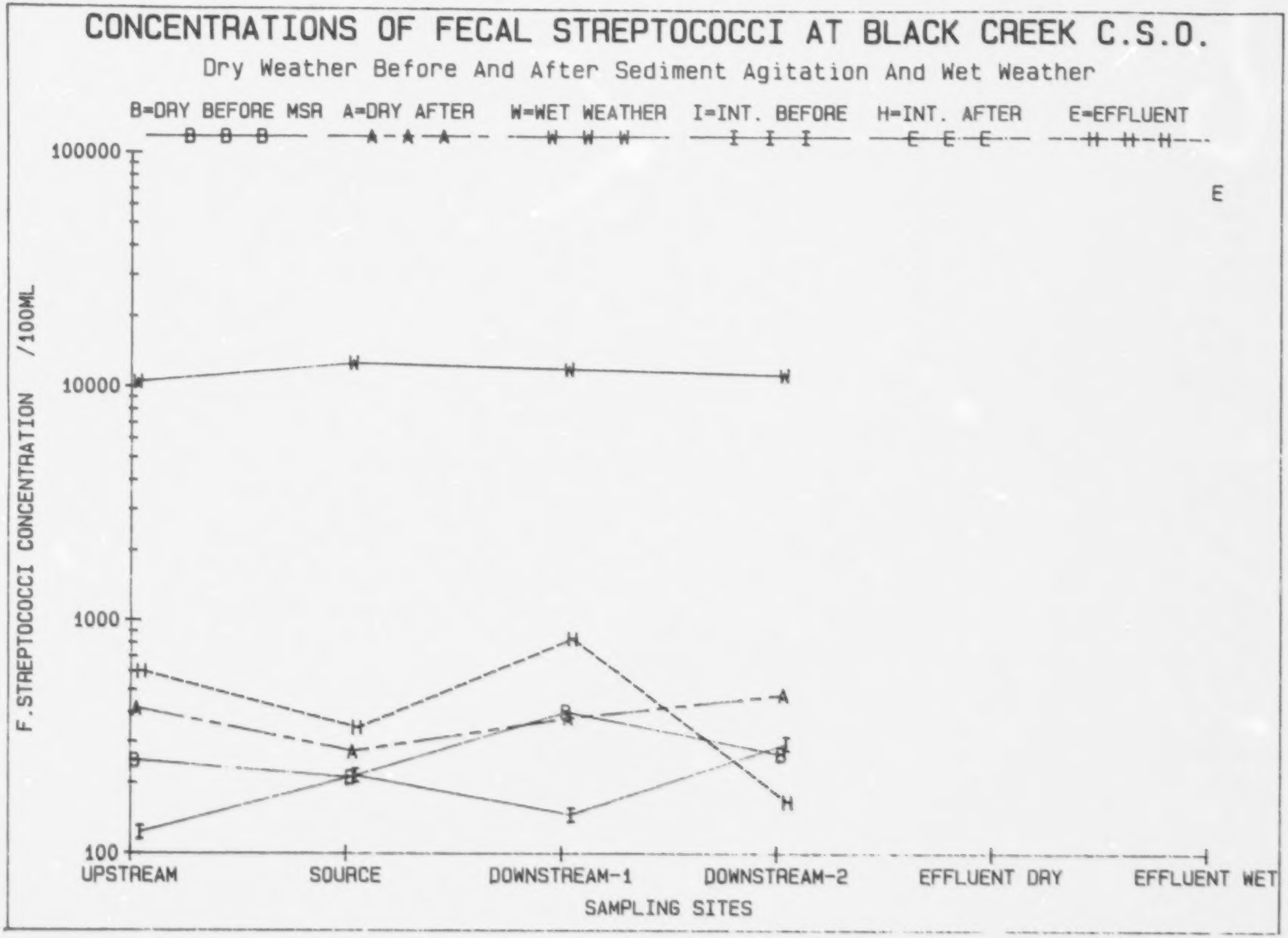


FIGURE 11: LEVELS OF SUSPENDED SEDIMENT AT THE ELHART DRIVE LOCATION UNDER DIFFERENT WEATHER CONDITIONS.

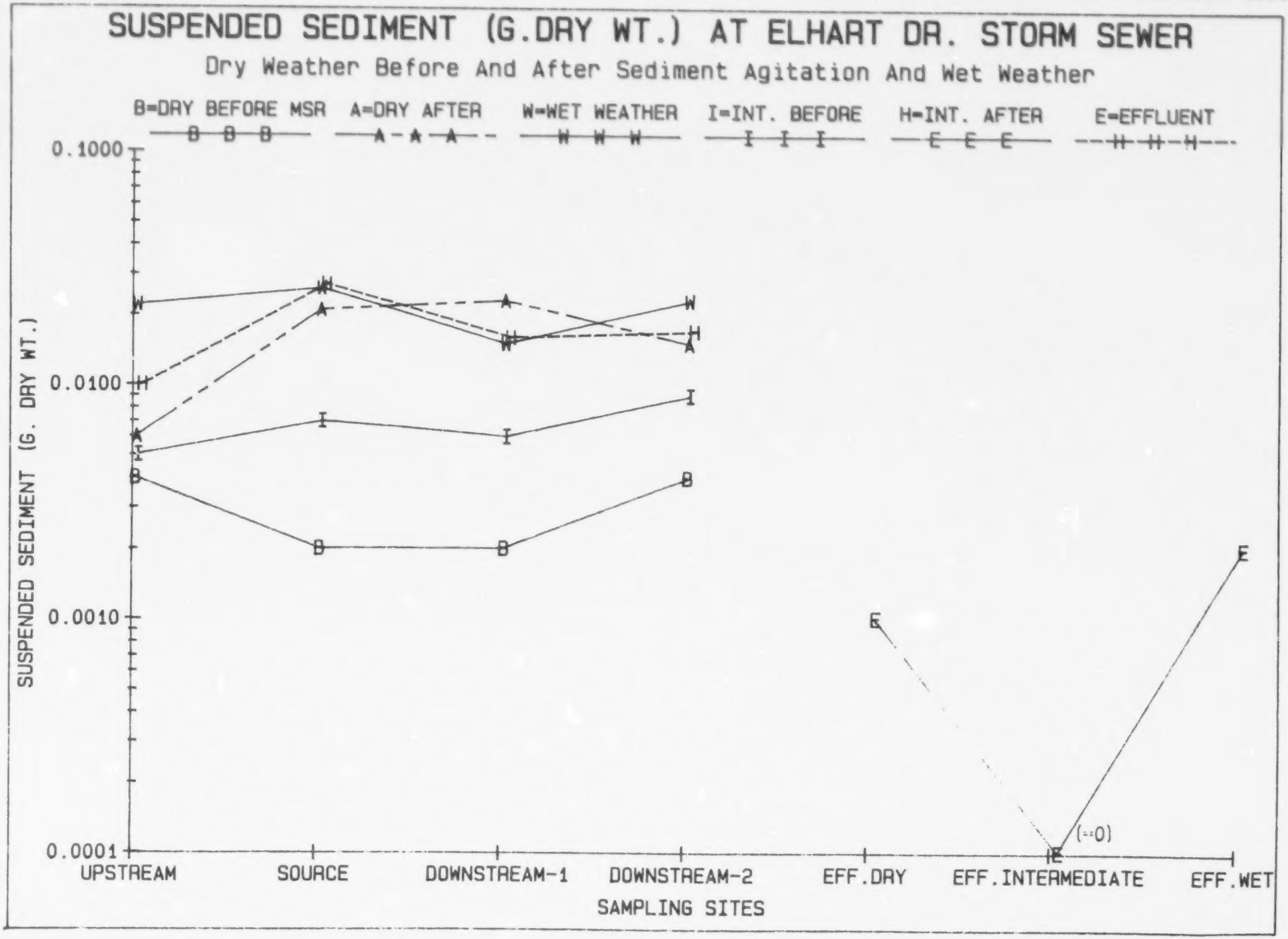


FIGURE 12: EFFECT OF WEATHER ON THE SUSPENDED SEDIMENT MEASUREMENTS AT THE JAMES GARDENS SITES

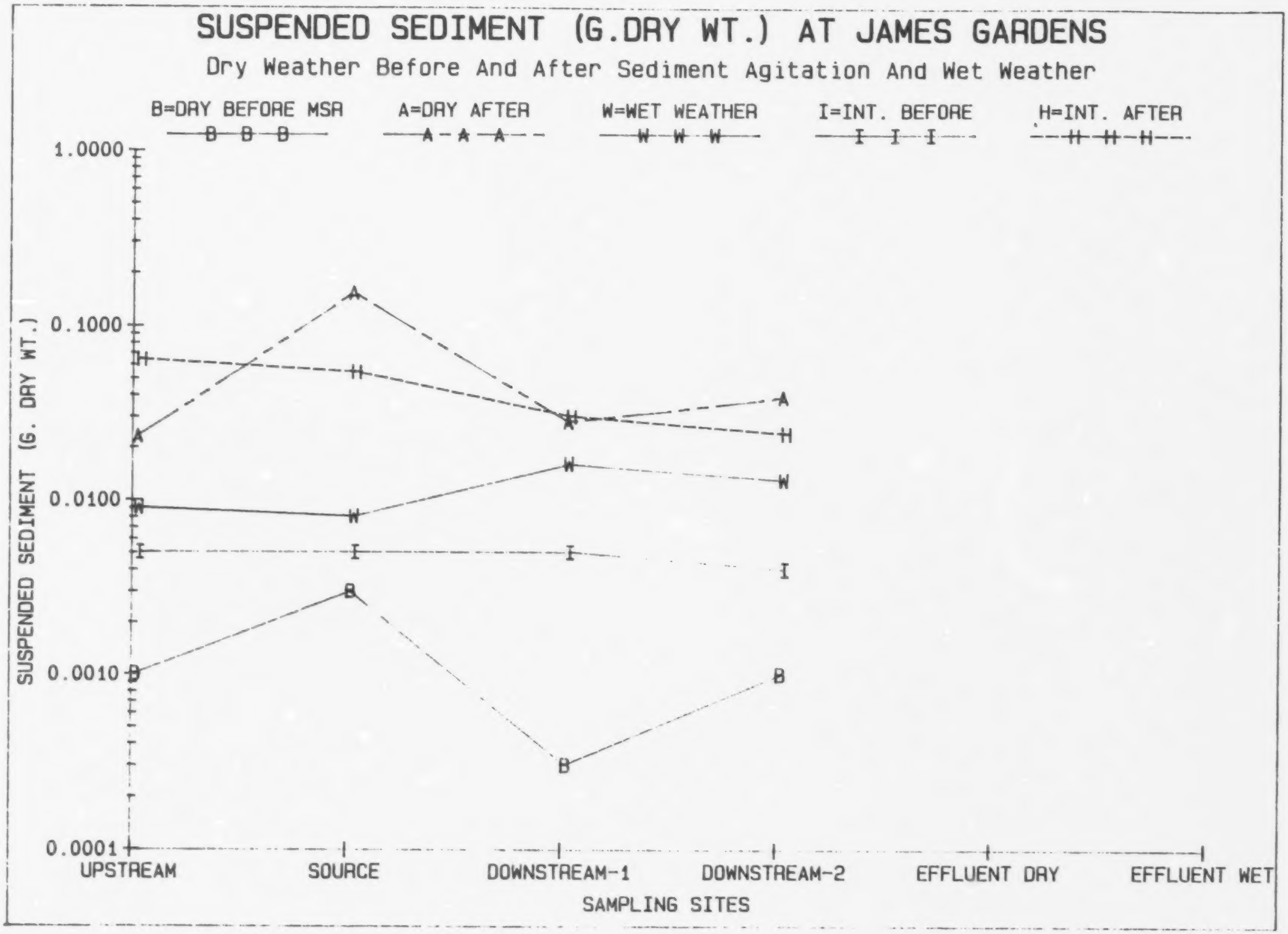


FIGURE 13: BLACK CREEK SUSPENDED SEDIMENT LEVELS UNDER DIFFERENT WEATHER CONDITIONS.

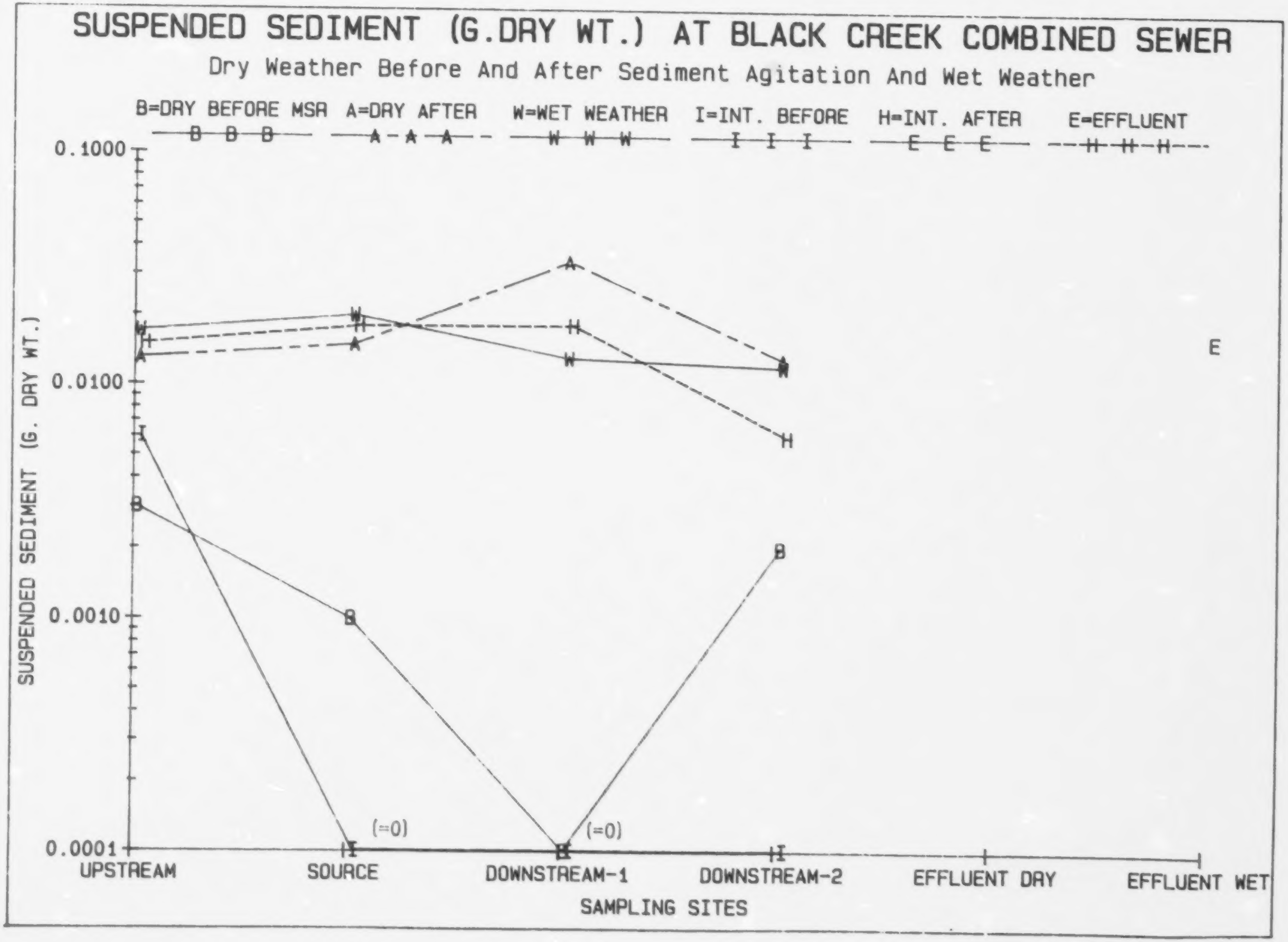


FIGURE 14: SUMMER DIE-OFF RATES OF FECAL INDICATOR BACTERIA AT THE ELHART DRIVE SITE

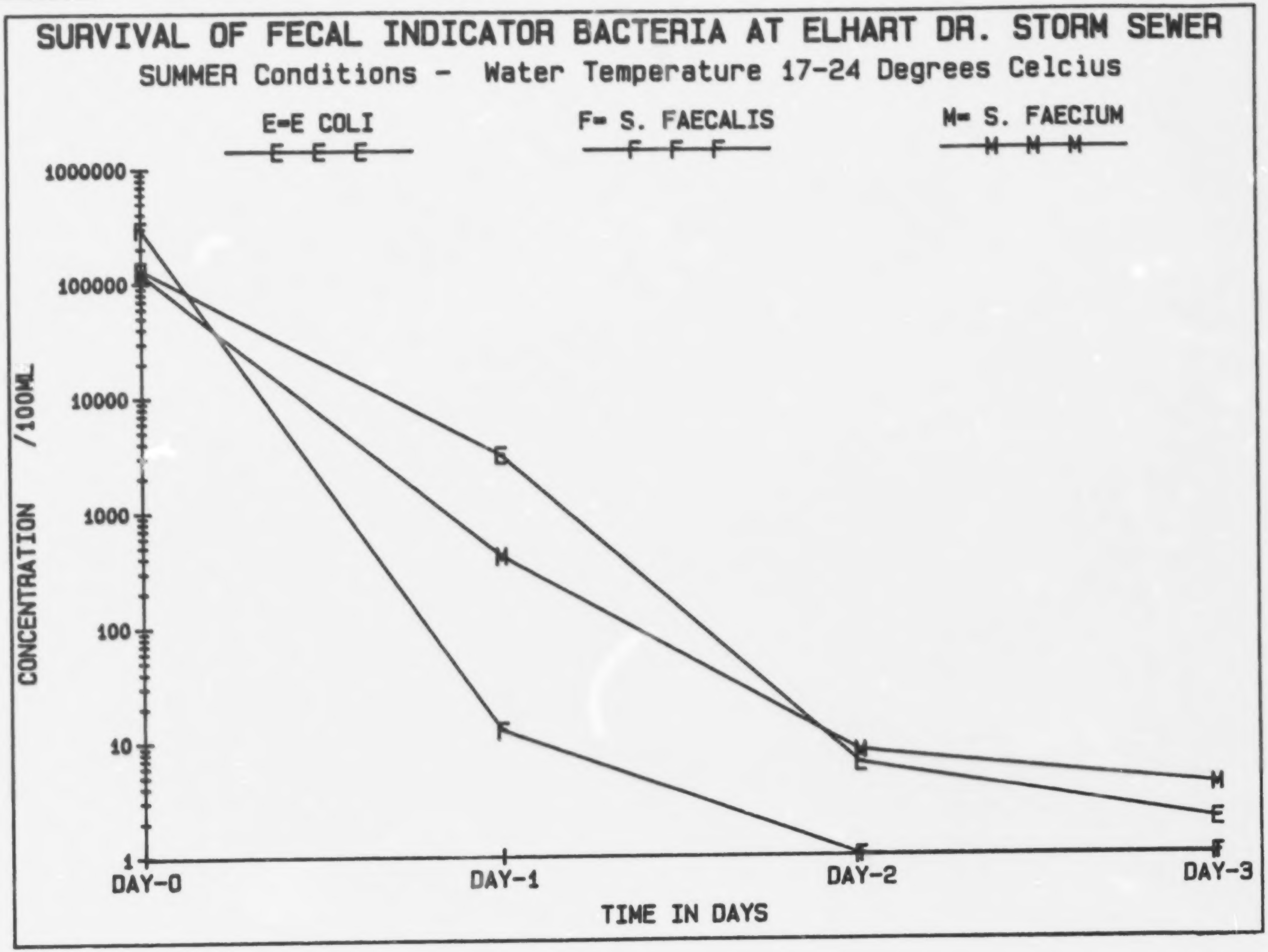


FIGURE 15: SURVIVAL RATES OF FECAL INDICATOR BACTERIA AT THE JAMES GARDENS LOCATION IN SUMMER

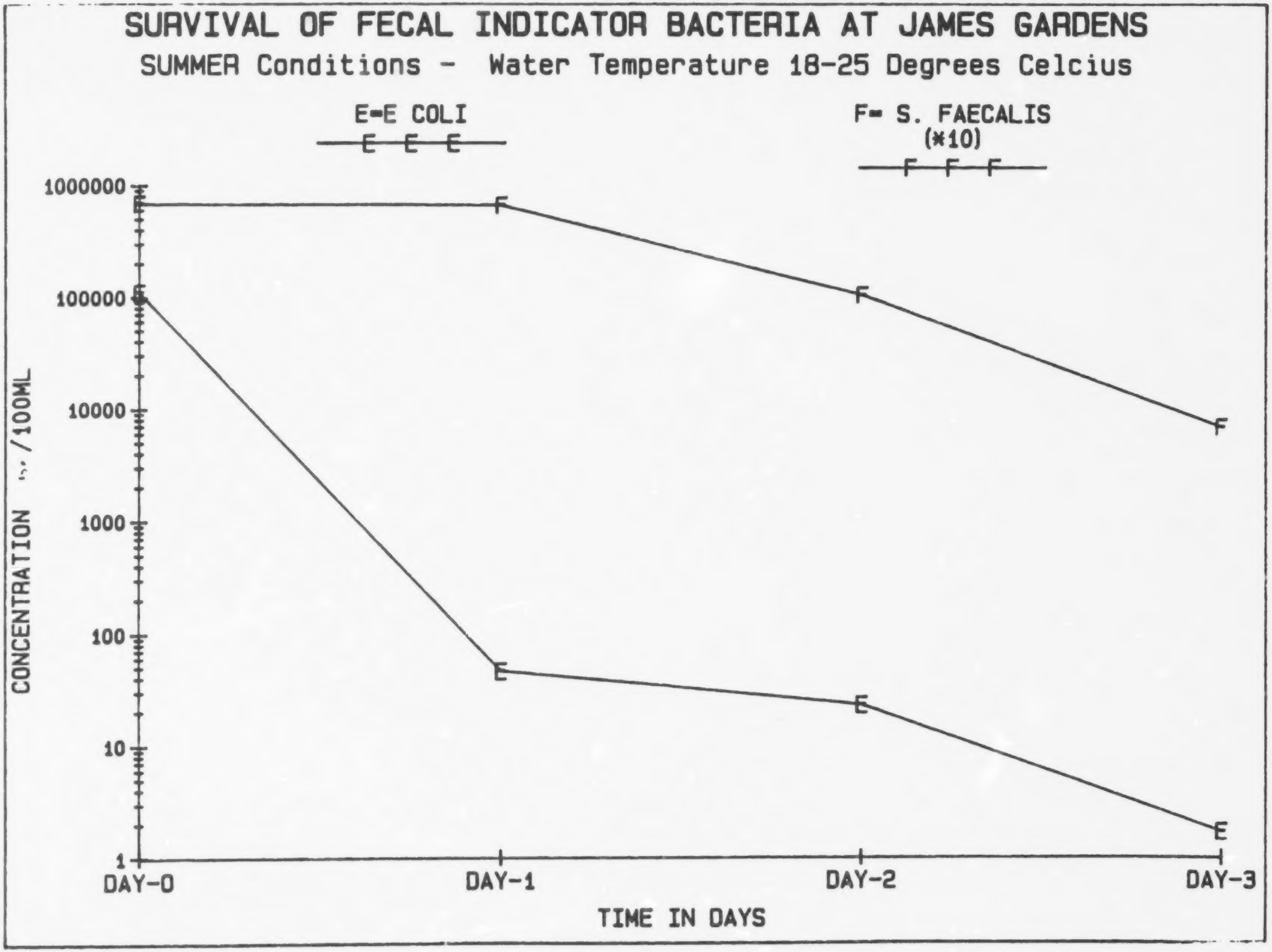


FIGURE 16: SUMMER SURVIVAL RATE OF FECAL INDICATOR BACTERIA AT THE BLACK CREEK SITE

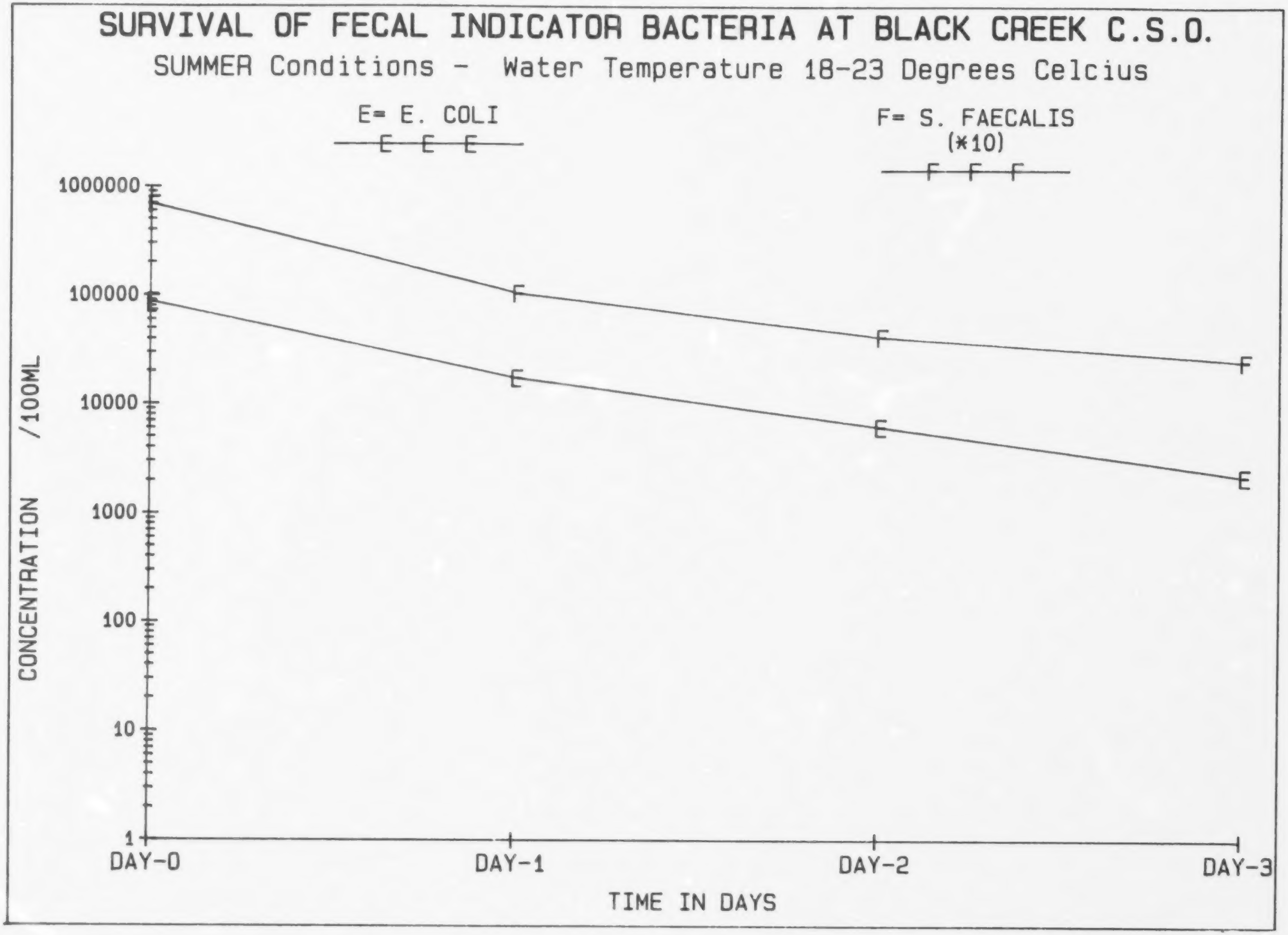


FIGURE 17: RATE OF SURVIVAL OF INDICATOR BACTERIA AT ELHART DRIVE IN WINTER

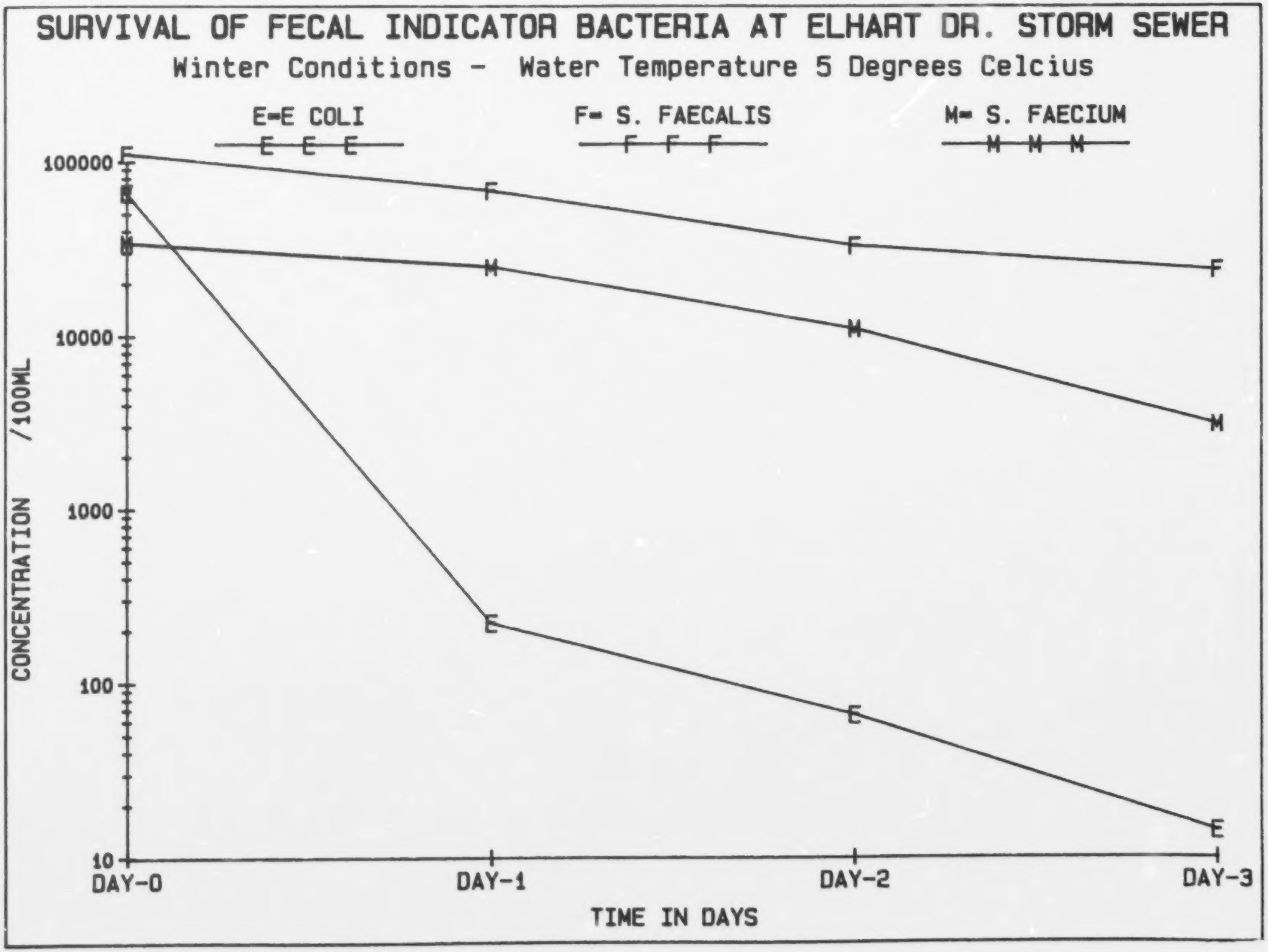


FIGURE 18: WINTER DIE-OFF RATES OF INDICATOR BACTERIA AT JAMES GARDENS

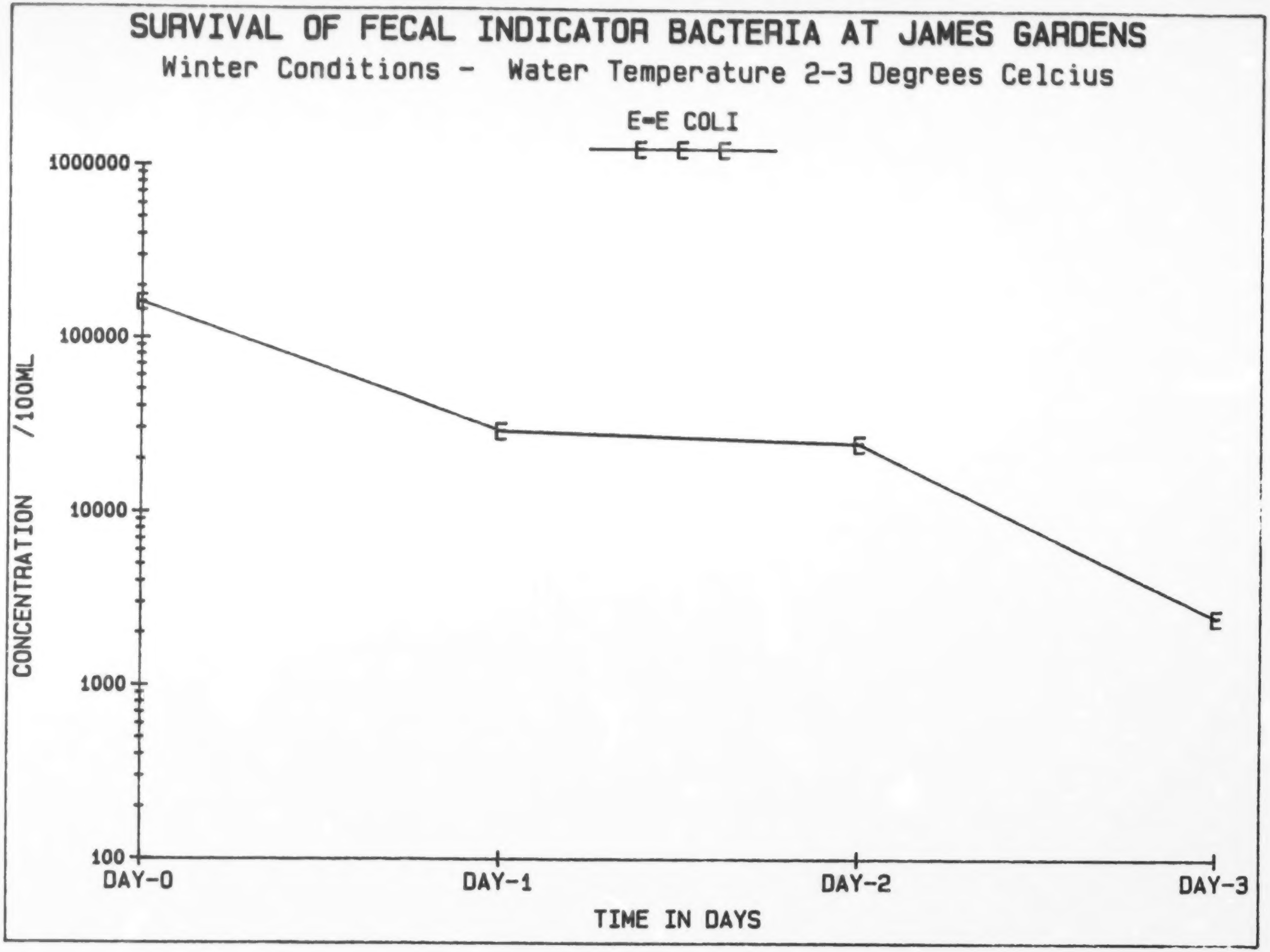


FIGURE 19: DIE-OFF RATE OF FECAL INDICATOR BACTERIA AT THE BLACK CREEK LOCATION IN WINTER

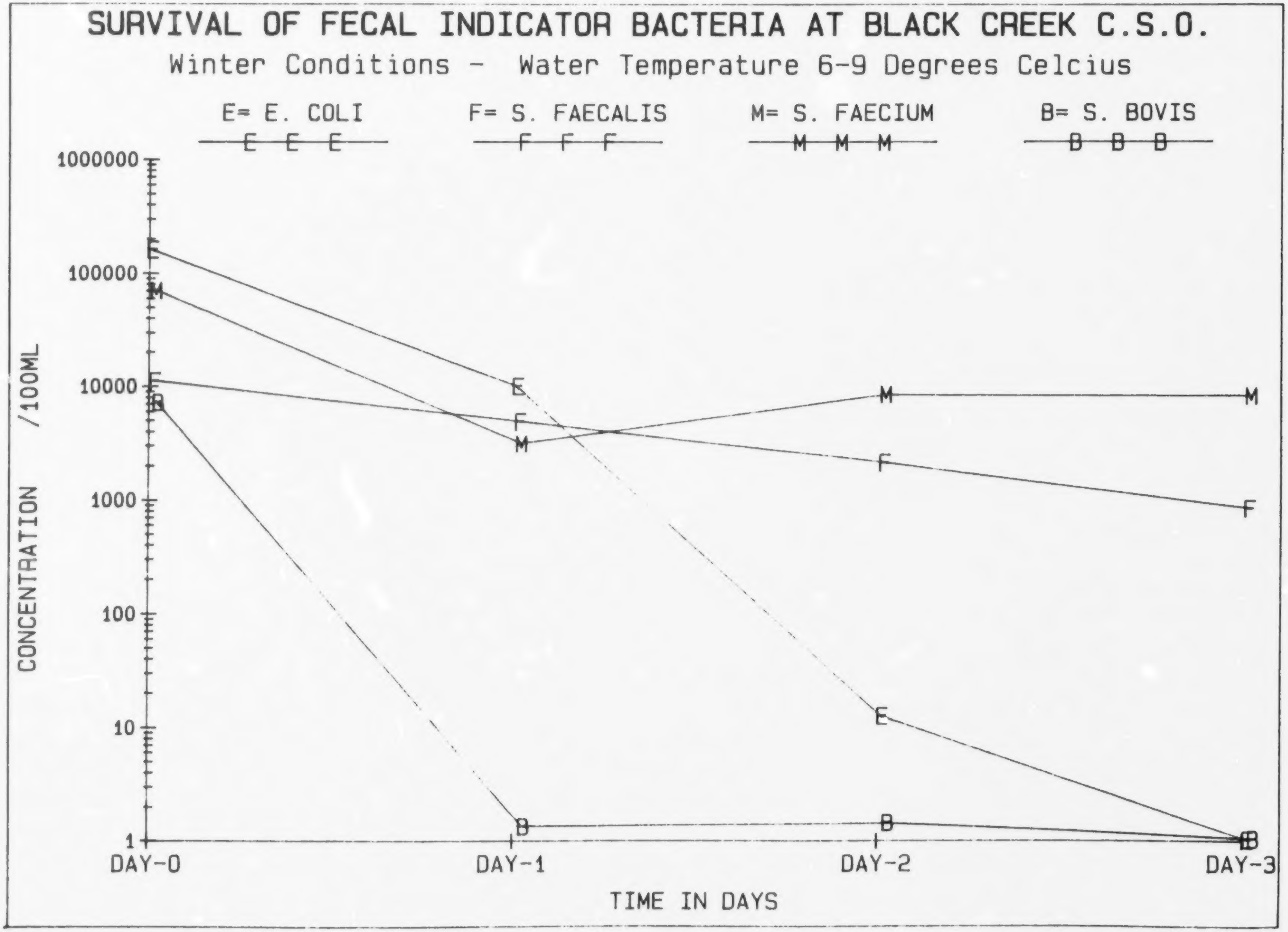


TABLE 1: Comparison of the Sampling Locations with Respect to Average Increases in Bacterial Concentration and Sediment Weight During Dry and Intermediate Weather (after Sediment Agitation) and from Dry to Wet Weather as well as Bacterial Die-off Rates During Summer and Winter Conditions

Location and weather condition	Parameter per 100 mls Sample				Flow Rate cm^3/sec.	Percent Die-off Rate in 24 hours					
	Sed. wt. (grams)	FC	EC	FS		E. coli summer	E. coli winter	S. faecalis summer	S. faecalis winter	S. faecium summer	S. faecium winter
Elhart Dr.						97.7	99.7	99.99	38.2	99.7	26.5
Δ Dry	0.013	341	203	136	1.660						
Δ Int.	0.011	626.5	446.5	150.5	2.570						
Δ Dry to Wet	0.019	3651	2337	1389	2.552						
Black Cr.						80.2	93.8	85.0	56.3	-	55.7
Δ Dry	0.017	330	168.5	104.5	0.152						
Δ Int.	0.013	613	508.5	288	0.221						
Δ Dry to Wet	0.014	12738	7628	11226	0.284						
James Gds.						99.96	81.9	2.9	-	-	-
Δ Dry	0.059	1074	801	120.5	2.593						
Δ Int.	0.038	949	680	243	3.193						
Δ Dry to Wet	0.010	2758	2181	1818	4.468						

REFERENCES

1. Sayler, G.S. 1985. Distribution and significance of fecal indicator organisms in the upper Chesapeake Bay. Appl. Microbiol. 30: 625-638.

2. Zobell, C.E. 1943. The effect of solid surfaces upon bacterial activity. J. Baterial. 46: 39-56.

3. Taga, N. and O. Matsuda, 1984. "Bacterial Populations Attached to Plankton, Detritus in Seawater" from Effect of the Ocean Environment on Microbial Activities. Colwell, R.R. Fd., University Park Press, p. 433-448.

4. Daniels, S.L. 1980. "Mechanisms Involved in Sorption of Microorganisms to Solid Surfaces" in Adsorption of Microorganisms to Surfaces Bitton and Marshall, Eds.

5. Hendricks, C.W. 1971. Increased recovery rate of salmonellae from stream bottom sediments versus surface waters. Appl. Microbial. 21: 379.

6. Van Donsel, D.J. and E.E. Geldreich. 1971. Relationships of Salmonella to fecal coliforms in bottom sediments. Water Res. 5 1079-1087.

7. Hendricks, C.W. 1971. Enteric bacterial metabolism of stream sediment eluates. Can. J. Microbial. 17: 551.

8. Gerba, C.P. and J.S. McLeod. 1976. Effect of Sediments on the survival of Escherichia coli in marine waters. Appl. Environ. Murobial. 32: 114.

9. Wood, E.J.F. 1965. Marine Microbial Ecology, Chapman and Hall Ltd., London, p. 24.

10. Gunnerson, C.G. 1963. Mineralization of organic matter in Santa Monica Bay, California in Symposium on Marine Microbiology, C.H. Oppenheimer Ed., Charles C. Thomas, Springfield Il., p. 641-653.

11. Geldreich, E.E. 1970. Applying bacteriological parameters to recreational water quality. J. Amer. Wat. Works Assoc. 62 (2): 113-120.

12. Wetzel, R.G. 1975. Limnology W.B. Saunders Co., Philadelphia, PA.

13. Avnimelech, Y., J.R. McHenry, and J.D. Ross. 1984. Decomposition of organic matter in lake sediments. Environ. Sei. and Technol. 18: 5-11.

14. Mitchell, R. and S. Yankofsky. 1969. Implication of a marine amoeba in the decline of Escherichia coli in seawater. Environ. See. Technol. 3: 574.

15. Brock, T.D. 1971. Microbial growth rates in nature. Bacterial. Revs. 35: 39.

16. Marshall, K.C. 1971. Sorptive interactions between soil particles and microorganisms in Soil Biochemistry Vol. II, A.D. McLaren and J.J. Skijens, Eds., Marcel Dekker, New York, p. 409-445.

17. Daniels, S.L. 1968. Separation of bacterial by adsorption onto ion exchange resins. Ph.D. Thesis, University of Michigan, Ann Arbor, Diss. Abstr. 29, 1336 B.

18. Berger, B.D., F.A. Butrico, H.J. Dunsmore, V.C. Lischer, H.F. Ludwig, F. Nevins, G.W. Reid, H. Romer and O.J. Sproul. 1970. Engineering Evaluation of Virus Hazards in Water. J. San. Eng. Div. 96: 111.

19. Matson, E.A., S.G. Hornor, and J.D. Buck. 1978. Pollution indicators and other microorganisms in river sediments. J. W.P.C.F. 39: R45-R63.

20. Erkenbrecher, C.W. Jr. 1980. Sediment bacteria as a water quality indicator in the Lynnhaven estuary. Virginia, U.S.A., VA Polytech Inst. State Univ. Water Resources Bull. 0 (126) I-X, 1-118.

21. Jenkins, A., M.J. Kirkly, A. McDonald, P. Waden, and D. Kay. 1984. Process based model of fecal bacterial levels in upland catchments. Water, Science and Tech. 16: 453-462.

22. Sayler, G.S. and C.M. Gilmour. 1978. Heteratrophic utilization of organic carbon in acquatic environments. J. Environ. Zual. 7 (3): 385-391.

23. Barnhart, C.L.H., and J.R. Vestal. 1983. Effects of Environmental Toxicants on Metabolic Activity of Natural Microbial Communities. Appl. and Environ. Microbiol. 46: 970-977.

24. Jameson, A.L.H. and J.R. Saxon. 1967. Field studies on the effect of daylight on mortality of coliform bacteria. Wat. Res. 1: 279-295.

25. Sjogren, R.E. and M.J. Gibson. 1981. Bacterial survival in a dilute environment. Appl. Environ. Microbial. 41: 1331-1336.

26. Hanes, N.B., G.A. Rohlich, and W.B. Sarles. 1966. The effect of temperature on the survival of indicator bacteria. New Eng. Wat. Works assoc. 80: 6-18.

27. McFeters, G.A. and D.G. Stuart. 1972. Survival of fecal coliform bacteria in natural waters. Field studies with membrane filter chambers.
Appl. Microbiol. 24: 805-811.

28. Geldreich, E.G., C.C. Best, B.A. Kenner and D.J. Van Donsel. 1968. Bacteriological aspects of stormwater pollution. Journal WPFC. 40(11): 1861-1872.

29. McNeil, A.R. 1985. Microbial water quality criteria: a review for Australia. Australian Water Resources Council Technical Paper No. 85: 1-447.

30. Mundt, J.O. 1963. Occurrence of enterococci on plants in a wild environment. Appl. Microbiol 11: 141.

31. Geldreich, E.E. B.A. Kenner and P.W. Kabler. 1964. Occurrence of coliforms, fecal coliforms and streptococci on vegetation and insects. Appl. Microbiol. 12: 63.

32. Geldreich, E.E. and B.A. Kenner. 1969. Concepts of fecal streptococci in stream pollution. J. Water Pollution Control Fed. 41: R336-352.

33. Gartner, Lee and Associates. 1983. Humber River and tributary dry weather outfall study. Toronto Area Watershed Management Strategy Study Technical Report #1. Ontario Ministry of Environment.

34. Dutka, B.J. and K.K. Kwan. 1980. Bacterial die-off and stream transport studies. Wat Res. 14: 909-915.

35. Geldreich, E.E. 1976. Fecal Coliform and fecal streptococci density relationships in waste discharges and receiving waters. CRC Critical Reviews in Environmental Control. 6(4): 349-369.

36. Sjogren, R.E. and M.J. Gibson.1981. Bacterial survival in a dilute environment. Appl. and Environ. Microbiol. 41(6): 1331-1336.

37. Kittrell, F.W. and S.A. Furfari.1963. Observations of coliform bacteria in streams. J. Water Poll. Control Fed. 35: 11.

38. Strecter, H.W. 1934. A formulation of bacterial changes occurring in polluted water. Sew. Works. J. 6: 208.

39. Van Donsel, D.J., E.E. Geldreich and N.A. Clark.1967. Seasonal variations in survival of indicator bacteria in soil and their contribution to stormwater pollution. Appl. Microbiol. 15: 1362-1370.

40. Evans, M.R. and J.D. Owens.1972. Factors affecting the concentrations of fecal bacteria in land-drainage water. J. Gen. Microbiol. 71: 477-485.

FEASIBILITY OF PLANT HARVESTING IN WATER QUALITY AMELIORATION AND NUTRIENT MANAGEMENT IN SHALLOW IMPOUNDMENTS

K. Clarke-Whistler[1], P.M. McKee[1] and G. Gaspardy[2]

[1]Beak Consultants Limited, Mississauga, Ontario
[2]Credit Valley Conservation Authority, Mississauga, Ontario

ABSTRACT

In a survey of southern Ontario reservoirs, eutrophication, as indicated by aquatic weed proliferation and/or algal blooms, was reported as a major management problem in over 80% of the impoundments. Aquatic plant harvesting may be useful in nutrient management in the reservoirs. In shallow impoundments where macrophyte biomass is high relative to the total volume of water, long-term harvesting, combined with control of nutrient sources, may effectively reduce loadings to downstream waters.

The Orangeville Reservoir, located at the headwaters of the Credit River, is highly eutrophic and contains heavy growth of aquatic macrophytes (Myriophyllum spp.). The Credit Valley Conservation Authority wishes to maintain or improve water quality and to improve the recreational potential of the reservoir. To this end, a mechanical plant harvesting program was initiated in 1984. This study evaluates the harvesting program and its potential for water quality improvement in Orangeville Reservoir.

Based on an estimated input-output budget for phosphorus and nitrogen, the reservoir was found to act as a nutrient sink. The major storage compartment for both nitrogen and phosphorus was the highly organic sediments. Net phosphorus retention by aquatic vegetation was small; therefore, it is unlikely that plant harvesting will reduce phosphorus concentrations in the water. This was attributed to most of the phosphorus used by plants being obtained from the sediments. There was no indication of phosphorus release during winter die-off, suggesting that phosphorus tied up in the plants is returned to the sediments. On the other hand, up to 67% of total nitrogen requirements of plants appeared to be met from the water column. Thus, harvesting represents a potentially effective method of nitrogen control.

The monitoring program has been expanded and is being continued through one full year (1986) using more intensive water quality sampling and streamflow measurements to refine the nutrient budgets and to determine harvesting optimality in biomass and nutrient removal in the reservoir. The 1986 program will be complete in December 1986, and will be reported in early 1987.

INTRODUCTION

Over recent years, major initiatives to reduce nutrient loading to the Great Lakes have been made in Canada and the United States. However, recent reports from both the Pollution from Land Use Activities Reference Group (PLUARG) and the Great Lakes Water Quality Agreement Board indicate low cost, technologically simple measures such as phosphate reduction in household detergents and upgrading of municipal sewage treatment plants may not be stringent enough to achieve the water quality objectives for the lower Great Lakes as stated in the agreement. In addition, multi-year studies show that loadings of inorganic nitrogen compounds to the lower Great Lakes basin are increasing (Taub, 1984). Aquatic plant harvesting represents a simple and relatively low cost method of nutrient management which has received little attention to date. Generally, nutrient loss due to plant removal is insignificant compared to the total nutrient budget in a waterbody, especially in the sediments. However, in some situations where macrophyte biomass is high in relation to the total volume of water (e.g., in shallow ponds and impoundments), long-term harvesting, combined with control of nutrient sources, may remove a sufficient portion of nutrients to significantly improve water quality.

During the 1950's and 1960's, numerous shallow reservoirs and ponds were created by dam construction in southern Ontario river systems to provide flood control in the spring and streamflow augmentation during summer low flows. A recent survey of such reservoirs currently being managed by conservation authorities, was conducted by Credit Valley Conservation Authority. Fifty-one impoundments ranging from 3.6 to 2,000 hectares, were identified. The majority of these reservoirs are shallow (<5 m) water bodies. Over 80% of the survey responses reported eutrophication as a major reservoir management problem. Common eutrophication indicators were aquatic weed proliferation and/or algae blooms. Many respondants reported high surface coverage by aquatic weeds and phosphorus concentrations in excess of Ontario Ministry of the Environment (MOE) guidelines. Weed control methods are employed in 29 of the 51 reservoirs. The most common control method is a combination of winter drawdown and chemical spraying. Mechanical weed harvesting was used in four reservoirs and was under consideration for an additional five reservoirs.

The Orangeville Reservoir, located on the northeastern edge of the Town of Orangeville at the headwaters of the Credit River, is typical of many southern Ontario reservoirs. It is highly eutrophic and contains heavy growths of aquatic macrophytes (*Myriophyllum* spp.). In 1984, a mechanical plant harvesting program was initiated as a weed control measure. In this study the harvesting program is evaluated, and the potential for water quality improvement at Orangeville Reservoir and in other similar impoundments in southern Ontario is discussed.

The specific objectives for monitoring weed harvesting in Orangeville Reservoir are:

- to permit site-specific assessment of potential improvements in water quality which might be expected as a result of weed harvesting; and
- to provide a preliminary mechanism for assessing the technical and economic feasibility of harvesting as a management tool for nutrient control in similar impoundments.

During 1984, a preliminary study was conducted to identify key components of the nutrient budget in Orangeville Reservoir. Major study components include:

- quantification of the nutrient budget through a steady-state input-output model;
- identification of major nutrient storage compartments within the reservoir; and
- evaluation of the effect of nutrient removal by plant harvesting.

METHODS

Study Area

The Orangeville Reservoir is located on the eastern edge of the Town of Orangeville, at the headwaters of the Credit River. It forms the major part of the 344 ha Orangeville Reservoir Conservation Area, operated by the Credit Valley Conservation Authority.

The reservoir is a multi-use facility, which provides:

- water storage for low flow augmentation to the Orangeville Water Pollution Control Plant, located 1.8 km downstream;
- a land and water-based recreational facility; and
- habitat for migratory waterfowl.

The reservoir was formed in 1967. Dykes were constructed at the north and south ends of the then existing cedar swamp to create an impoundment with a maximum surface area of 173 ha. Flow control and overflow structures are located at the south dyke (Figure 1).

The reservoir drainage basin is 27.2 km^2. Four springfed streams, the largest being Monora Creek, flow into the reservoir and a fifth spring is located under it. Total water capacity is 3.08×10^6 m^3. A volume of 1.57×10^6 m^3 has typically been maintained for flow augmentation. Dam operation was originally scheduled to achieve a minimum year round flow of 0.28 m^3/sec. However, the reservoir policy was modified in 1978 to facilitate water-based recreational activity and enhance waterfowl habitat. During the summer, the control valve is closed and high water levels are maintained. Flow to the Credit River occurs as seepage (about 0.014 to 0.057 m^3/sec) through the dyke. During August through November, the valve is opened to allow higher flows for low flow augmentation. By the end of November, the reservoir is at its lowest level. It is maintained at this level through the winter to maximize storage capacity for the spring thaw (IEC, 1981).

The reservoir is shallow with extensive marshland. Open water areas are approximately 2.7 to 3.4 m deep. The average depth of the reservoir, including the marsh, is 1.5 m. A deep (7.6 m) hole occurs in the eastern arm (Figure 1). During the summer months, the entire surface of the reservoir is covered by extensive aquatic weed growth. The dominant species are Myriophyllum spp. (excalbescens and/or spicatum).

Sampling Methods and Analysis

Much of the data used in calculating nutrient budgets were obtained from the unpublished and published reports referenced in each section. However, a small number of samples were collected from the reservoir to verify historical data. Samples of water, macrophytes and sediments were collected during August 1984. An additional set of water samples were collected in October 1984. As shown in Figure 1, six sampling stations were located at various locations in and around the reservoir. These included shallow and deep locations, harvested and unharvested sites, inflows and the outflow. At each reservoir sampling station, vertical temperature, pH, conductivity and oxygen profiles were taken. Water samples were collected from 0.5 m below the surface and 0.5 m above the bottom using a Van Dorn sampler. During the August sampling period, a large (10 L) water sample was collected from each station in order to determine suspended particulate (seston) concentrations. Surface sediment samples (10 cm) were collected from each reservoir station by Ekman dredge. Triplicate vegetation samples (0.25 m^2) were collected from each reservoir station by SCUBA diver. All above and below ground parts were collected.

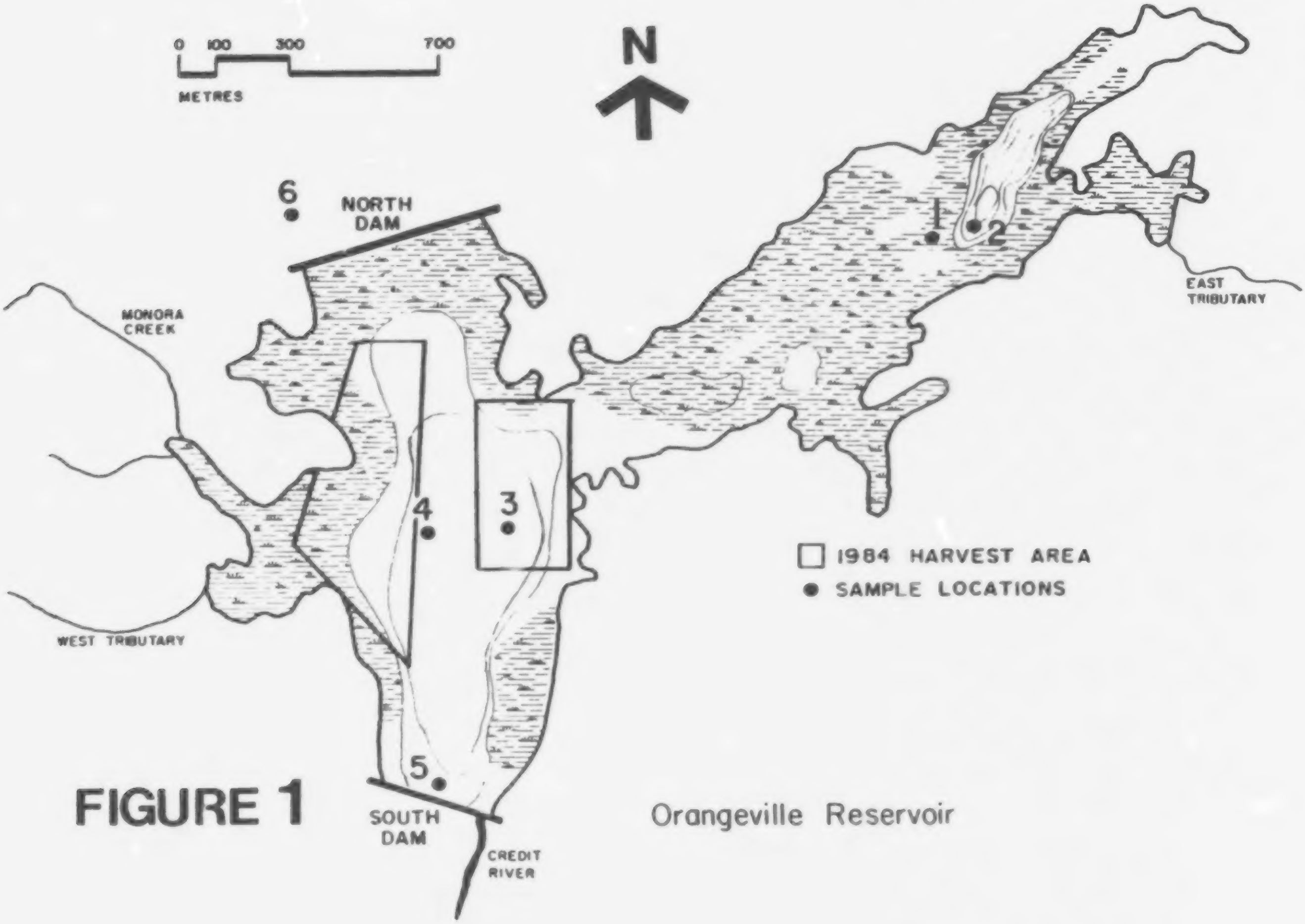


FIGURE 1

Orangeville Reservoir

Nutrient analysis of water, vegetation and sediment samples were performed at the Laboratory Services Branch of the MOE. Analytical methods are outlined in the MOE Outlines of Analytical Methods (1975).

RESULTS

Calculation of Nutrient Budget

A preliminary nutrient budget for phosphorus and nitrogen was determined using a steady-state input-output model of the form:

$$\text{Nutrient Storage} = \text{Input-Output}$$

Input sources include atmospheric deposition and surface water inflow. Overland flow and groundwater are considered negligible given the small drainage area. Output is based on dam outflow. Losses via seepage are considered insignificant. Major components of the nutrient budget are discussed in the following sections.

Atmospheric Deposition

Annual loadings of total phosphorus (TP) and total nitrogen (TN) via precipitation and dry deposition were calculated according to the formula:

$$\begin{aligned}\text{Input atmospheric} &= (\text{ nutrient}_{\text{precipitation}} + \text{nutrient}_{\text{dry deposition}}) \\ &\quad \times \text{ volume of precipitation} \times \text{surface area of reservoir}\end{aligned}$$

All loading calculations assume a reservoir surface area of 1.6×10^6 m^2.

Precipitation inputs are summarized in Table 1. Seasonal average rainfall values are based on long-term averages recorded at the Orangeville MOE monitoring station (AES, 1982). Nutrient concentrations in precipitation are from the Acidic Precipitation in Ontario Study (APIOS) station at Palmerston, Ontario. This station is within 80 km of Orangeville and receives precipitation from similar sources. Concentration data are based on monthly samples collected over the fifteen month period from September 1980 - December 1981 (Chan et al., 1983).

Dry deposition values for nitrogen are derived from isopleths of NO_3 deposition for southern Ontario (M. Lusis, unpublished). A value of 0.6 $g/m^2/yr$ was interpolated for the Orangeville area. This value is considered to more accurately represent total nitrogen deposition and is included as such in loading calculations (M. Lusis, pers. comm.).

TABLE 1: NUTRIENT INPUTS TO ORANGEVILLE RESERVOIR VIA ATMOSPHERIC DEPOSITION
(Reservoir surface area = $1.6 \times 10^6 m^2$)

A. Wet Deposition

	Total Precipitation (mm)	Volume of Precipitation ($\times 10^5 m^3$)	Nutrient Concentration (g/m^3)				Nutrient Loading (kg)			
			TP	TKN	NO_3	NH_4	TP	TKN	NO_3	NH_4
Spring	201.6	3.23	0.0171	1.211	0.787	1.055	5.52	390.6	254.4	340.3
Summer	231.8	3.71	0.0176	0.887	0.536	0.680	6.53	329.0	198.4	252.2
Fall	223.8	3.58	0.0270	0.901	0.501	0.672	9.67	322.6	179.2	240.6
Winter	185.6	2.97	0.0050	0.840	0.636	0.648	1.48	249.4	188.9	192.4
Total	842.8	13.49					23.20	1291.6	820.9	1025.5

B. Dry Deposition

Total Phosphorus = $0.0385\ g/m^2/yr \times 1.6 \times 10^6 m^2 = 61.6$ kg

Total Nitrogen (as NO_3) = $0.6\ g/m^2/yr \times 1.6 \times 10^6 m^2 = 960$ kg

C. Total Nutrient Loading

Total Phosphorus = $(\text{Total Phosphorus})_{wet} + (\text{Total Phosphorus})_{dry}$
= 23.20 + 61.60
= 85 kg

Total Nitrogen = $(\text{Total TKN} + \text{Total } NO_3)_{wet} + (\text{Total Nitrogen})_{dry}$
= 1291.6 + 820.9 + 960
= 3070 kg

Phosphorus deposition was back-calculated and extrapolated from a long-term bulk depositional value of 35 mg/m^2/yr TP, measured for the Muskoka-Haliburton area (P. Dillon, pers. comm). Bulk nutrient deposition would be expected to be significantly higher than this value in an agricultural area such as that surrounding Orangeville. Based on comparison with nitrogen deposition isopleths, a total of 53 mg/m^2/yr TP was assumed to be appropriate for Orangeville. By subtracting the calculated TP deposition via precipitation (14.5 mg/m^2/yr), a value of 38.5 mg/m^2/yr TP was derived for dry deposition.

Based on the above calculations, summarized in Table 1, totals of 3,070 kg of nitrogen and 85 kg of phosphorus annually are estimated to enter the Orangeville Reservoir via atmospheric deposition.

Surface Inflow

Surface inflow is calculated as:

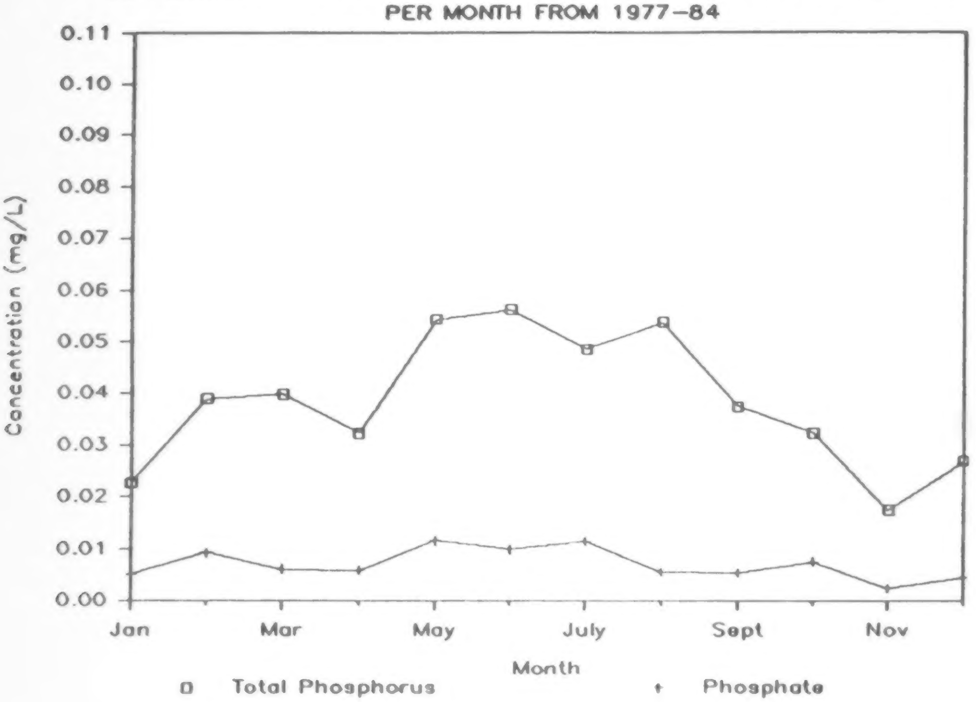
$$\text{Surface Inflow} = \underset{(\times 10^5 m^3)}{\text{volume inflow}} \times \underset{(g/m^3)}{\text{nutrient concentration}}$$

As shown in Figure 1, surface inflow to Orangeville Reservoir is via four small springfed streams. During August 1984, stream inflow was monitored by CVCA for a two week period, and an average daily discharge value of 0.0830 m^3/sec was derived. Streamflow data for the remainder of the year were extrapolated from monitored streams which displayed similar discharge or water quality characteristics (Tables 2 and 3). Composite nutrient samples were collected during the same time period.

Stream discharge was calibrated against the Schomberg River (Water Survey of Canada,1983; Station Number O23COAO). This small stream has a drainage area of 42.9 km^2 and a basin comprised primarily of farmland. Flow characteristics and inflow calculations are shown in Table 2.

Nutrient samples were collected at Monora Creek in August and October. Data for the remainder of the year were extrapolated from average concentrations in the Orangeville Reservoir outflow (Table 3; Figure 2). August and October inflow concentrations are within the 95% confidence interval of mean outflow concentrations. Based on these calculations the total nutrient input to the reservoir via inflow is 1.46 x 10^4 kg TN and 433 kg TP.

FIGURE 2 NUTRIENT CONCENTRATIONS IN ORANGEVILLE RESERVOIR OUTFLOW


AVERAGE PHOSPHORUS CONCENTRATION

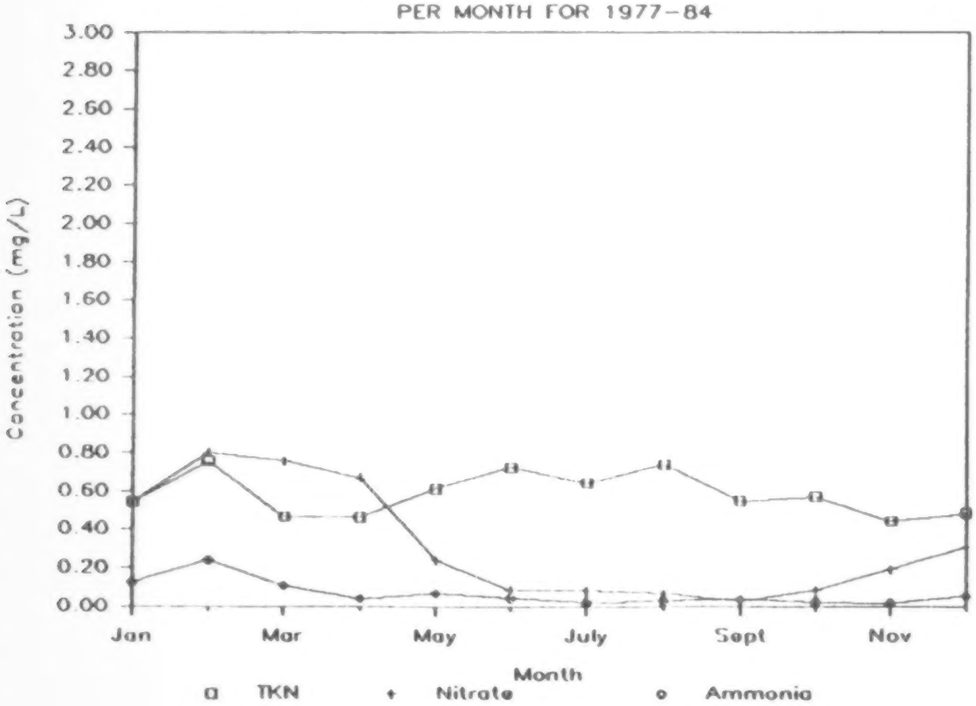

AVERAGE NITROGEN CONCENTRATION

TABLE 2: DERIVATION OF NUTRIENT INPUTS TO ORANGEVILLE RESERVOIR VIA SURFACE INFLOW

A. Discharge Data for Schomberg River

Month	Mean Daily Discharge (cms)	Monthly Volume ($\times 10^5 m^3$)	Calculated Inflow to Orangeville Reservoir ($\times 10^5 m^3$)
January	0.228	6.11	7.14
February	0.326	7.89	9.22
March	0.999	26.75	36.18
April	0.815	21.12	28.52
May	0.238	6.37	7.45
June	0.115	2.98	3.48
July	0.100	2.68	3.13
August	0.071 (0.083*)	1.90	2.57*
September	0.077	2.00	2.34
October	0.146	3.91	4.57
November	0.213	3.52	4.11
December	0.270	7.23	8.45
		49.38	58.06

B. Nutrient Load To Orangeville Reservoir Via Inflow (kg)

	TP	TKN	NO_3**
January	16.4	387.7	389.1
February	36.0	697.0	739.4
March	144.7	1,689.6	4,652.7
April	91.3	1,326.2	1,908.0
May	40.2	458.2	180.3
June	19.5	252.3	30.3
July	15.0	200.6	26.3
August	13.9	190.7	17.7
September	8.7	128.7	7.0
October	14.6	260.9	6.9
November	7.0	180.8	80.1
December	22.8	410.7	262.8
	430	6,183.5	8,300.8

* = Orangeville Reservoir

** = $NO_3 + NO_2$

Annual Nutrient Load via Inflow:

Total Phosphorus = 430 kg
Total Nitrogen = 1.45×10^4 kg

TABLE 3: ANNUAL NUTRIENT LOADING TO THE CREDIT RIVER VIA OUTFLOW FROM ORANGEVILLE RESERVOIR

	Mean Daily Discharge (cms)	Monthly Volume (x $10^5 m^3$)	Mean Nutrient Concentration (1977- 1984) (g/m^3)			Nutrient Loading (kg)		
			TP	TKN	NO_3*	TP	TKN	NO_3*
January	0.318	8.52	0.023	0.543	0.545	19.60	462.6	464.7
February	0.242	5.85	0.039	0.756	0.802	22.82	442.3	469.0
March	0.205	5.49	0.040	0.467	1.286	21.96	256.4	706.1
April	0.227	5.88	0.032	0.465	0.669	18.82	273.4	393.3
May	0.698	18.70	0.054	0.615	0.242	100.98	1150.1	451.6
June	0.211	5.47	0.056	0.725	0.087	30.63	396.6	47.6
July	0.208	5.57	0.048	0.641	0.084	26.74	357.0	47.0
August	0.220	5.89	0.054	0.742	0.069	31.81	437.0	40.4
September	0.214	5.55	0.037	0.550	0.030	20.54	305.3	16.7
October	0.205	5.49	0.032	0.571	0.015	17.57	313.5	8.0
November	0.288	7.46	0.017	0.443	0.195	12.68	330.5	145.8
December	0.284	7.61	0.027	0.486	0.311	20.55	369.8	236.3
			$\bar{x}$ 0.038	$\bar{x}$ 0.584	$\bar{x}$ 0.361			
Annual Loading via Outflow:						345	5,094	3,026

Total Phosphorus = 344.7 kg

Total Nitrogen = 8,120.9 kg

* = $NO_3 + NO_2$

Outflow

Surface outflow was calculated from monthly means of historical discharge and water quality data collected at the reservoir outflow dam (Table 3; Figure 2). Outflow was calculated as:

$$\text{Surface Outflow} = \underset{(\times\ 10^5 m^3)}{\text{volume outflow}} \times \underset{(g/m^3)}{\text{nutrient concentration}}$$

Since the dam outflow is regulated, discharge does not follow typical seasonal patterns associated with spring melt. Maximum outflow occurs in May, approximately two months after the major spring runoff, and winter discharge values are higher than might normally be expected as a result of low flow augmentation.

Average monthly nutrient concentrations are shown in Figure 2. Average monthly total phosphorus concentrations range between 0.017 and 0.056 mg/L, with an annual average of 0.038 mg/L. Maximum concentrations generally occur during summer. Bioavailable phosphate averages less than 0.010 mg/L and shows little annual variation.

TKN concentrations show a similar seasonal pattern similar to that of TP concentrations, averaging 0.584 mg/L over the year. The bioavailable forms of nitrogen, nitrate and ammonia, show seasonal patterns associated with uptake and release by biota. Concentrations of both forms are lowest during the spring and summer months, when primary and secondary production is high. High concentrations during the fall and winter months (up to 1.286 mg/L) may be attributable to releases resulting from plant die-off and incorporation into the anaerobic sediments.

Based on the data in Table 3, annual nutrient loadings to the Credit River via outflow from the Orangeville Reservoir are calculated as 345 kg total phosphorus and 8120 kg total nitrogen.

Nutrient Budget

Based on the calculations in the preceding sections, the nutrient budget for Orangeville Reservoir is:

$$\begin{aligned}\text{Reservoir Storage of Total Phosphorus} &= TP_{input} - TP_{output} \\ &= \underset{(\text{atmos})}{85\ \text{kg}} + \underset{(\text{inflow})}{430\ \text{kg}} - \underset{(\text{outflow})}{345\ \text{kg}} \\ &= 170\ \text{kg}\end{aligned}$$

$$\text{Reservoir Storage of Total Nitrogen} = \underset{\text{(atmos)}}{3{,}070\ \text{kg}} + \underset{\text{(inflow)}}{1.45 \times 10^4\text{kg}} - \underset{\text{(outflow)}}{8{,}120\ \text{kg}}$$

$$= 9{,}450\ \text{kg}$$

$$\text{Reservoir Storage of Nitrate} = \underset{\text{(atmos)}}{1{,}780\ \text{kg}} + \underset{\text{(inflow)}}{8{,}300} - \underset{\text{(outflow)}}{3{,}026}$$

$$= 7{,}054\ \text{kg}$$

In light of the simplified nitrogen cycle used and the inaccuracy of measurement associated with inflow and atmospheric deposition, errors of 20 to 30% may be associated with these budgets. Nonetheless, on an annual basis the reservoir appears to act as a nutrient sink, rather than a source. The calculated budgets indicate that approximately 33% of the net annual total phosphorus input and 55% of the total nitrogen input are retained.

Nutrient Storage

The effectiveness of plant harvesting as a means of water quality improvement depends on the total nutrient load removed from the water by macrophytes. As indicated in the previous sections, a significant proportion of the nitrogen and possibly some of the phosphorus entering the reservoir is retained. Nutrient storage compartments within the reservoir include aquatic macrophytes, sediments and the water column. Fish and aquatic macroinvertebrates are considered negligible. The relative importance of the major storage compartments are discussed in the following sections.

Macrophytes

The total biomass of macrophytes, including above and below ground parts is calculated in Table 4. Total biomass in shallow waters (< 2.5 m) ranges between approximately 920 and 2,700 g/m^2. Biomass was significantly lower in samples collected at depths of 5 m, confirming reports of maximum Myriophyllum productivity at depths of less than 4 m (Grace and Tilly, 1976). In calculating total standing crop, it was assumed that 5% of the reservoir bottom is greater than 5 m deep (Figure 2), and that Myriophyllum bottom coverage was 50% (Table 4). Thus a total biomass of 5.02×10^5 kg dry weight was derived. Average nutrient concentrations in macrophytes were 0.21% and 2.09% for total phosphorus and total nitrogen, respectively. Thus the aquatic vegetation contains an estimated total of 1,053 kg of phosphorus and 1.05×10^4 kg of nitrogen (Table 4).

TABLE 4: TOTAL NUTRIENT CONTENT OF AQUATIC MACROPHYTES IN ORANGEVILLE RESERVOIR

Location	Depth (m)	Biomass (g/m^2 dry weight)	Total Nitrogen (%)	Total Phosphorus (%)
Station 1	1.2			
		921.8	1.89	0.12
Replicate - 1		1,768.2	1.77	0.12
- 2		1,410.0	1.72	0.10
- 3		$\bar{x}$ Total = 1,366.7	$\bar{x}$ = 1.79	$\bar{x}$ = 0.11
		$\bar{x}$ Above-ground = 820.0		
Station 2	5			
Replicate - 1		6.2	2.85	0.22
- 2		12.2	3.26	0.41
- 3		4.2	3.00	0.26
		$\bar{x}$ Total = 7.5	$\bar{x}$ = 3.04	$\bar{x}$ = 0.30
		$\bar{x}$ Above-ground = 4.5		
Station 3	2.1 (cutover)			
Replicate - 1		284.0	1.83	0.19
- 2		180.0	1.93	0.20
- 3		168.0	1.40	0.15
		$\bar{x}$ Total = 210.7	$\bar{x}$ = 1.72	$\bar{x}$ = 0.18
		$\bar{x}$ Above-ground = 126.4		
Station 4	2.1			
Replicate - 1		2,660.0	1.41	0.18
- 2		1,960.0	1.91	0.27
- 3		1,180.0	2.12	0.29
		$\bar{x}$ Total = 1,933.0	$\bar{x}$ = 1.81	$\bar{x}$ = 0.25
		$\bar{x}$ Above-ground = 1,160.0		

Average above-ground biomass for non-cutover areas = (820.0 + 1,160.0) x 95% + (4.5) 5%
(weighted by depth) = 627.1 g/m^2 dry weight

Total biomass assuming 50% bottom coverage = 5.02 x 10^5 kg
(bottom area - 1.6 x 10^{6}m^2)

Total Phosphorus = 1,053 kg
Total Nitrogen = 1.05 x 10^4 kg

Sediment

Surface (10 cm) sediments are highly organic and largely composed of decaying Myriophyllum. Dry bulk densities are low (2.00 g/cm^3) reflecting the predominance of the organic material. Average nutrient contents in the top 10 cm were 0.13% and 1.56% for total phosphorus and total nitrogen, respectively. Based on these concentrations, and the sediment bulk density, a total of 4.2×10^4 kg total phosphorus and 5.0×10^5 kg total nitrogen are contained in the surface sediments. Sedimentation rates would need to be measured to determine annual sedimentary loss of nutrients.

Water

Nutrient contents in unfiltered water samples collected during this study fall within historical ranges reported for the reservoir outflow. In calculating nutrient storage in the water column, historical water quality data collected at the reservoir outflow between 1977 and 1984 were used. The average TP concentration in the reservoir, over these eight years, was 0.038 mg/L, whereas the average TN concentration was 0.945 mg/L. The total water volume in the reservoir, based on a surface area of 1.6×10^6 m^2, is 1.24×10^6 m^3 (1,939 acre-feet) (M.M. Dillon Ltd., 1966). Thus the total nutrient content of the water column is 47 kg TP and 1,170 kg TN.

Suspended particulate concentrations in the outflow typically range between 1 and 15 mg/L. However, sampling conducted during this study indicated that wind turbulence resulted in higher particulate levels within the reservoir. Particulate concentrations in samples collected in August and October, 1984, averaged approximately 25 mg/L. Comparisons between nutrient concentrations of filtered and unfiltered waters indicated that 28% of TP and 25% TN was associated with suspended particulates. Therefore, a total nutrient load of 1.3 kg TP and 293 kg TN is associated with the suspended solids and the remainder (45.7 kg and 879 kg, respectively) is contained in dissolved forms.

Biomass Removal by Plant Harvesting

Weed harvesting began in late July, 1984 and continued, five days per week until 25 September. Total cutting time was 178 hours. Because 1984 was the first year of weed cutting, the working season was short and harvesting efficiency was low. Productivity rates are expected to increase substantially during subsequent harvesting seasons as operators gain better understanding of the system.

The total biomass removed via harvesting was calculated based on the number of harvester loads times the average load weight (1,000 lbs) (Table 5). Thus an estimated total biomass of 2.13×10^5 kg wet weight was removed. This is equivalent to 1.85×10^4 kg dry matter, based on an average moisture content of 91.3% obtained in the calculation of the total reservoir biomass. Assuming TP and TN content of 0.21% and 2.09% respectively, a total of 39 kg TP and 390 kg TN were removed via plant harvesting. These loads represent approximately 3.7% of the total nutrients contained in the aquatic vegetation.

The total plant biomass which might ultimately be removed from the reservoir once harvesting efficiency has been optimized may be roughly estimated from results of a similar harvesting operation conducted in Lake Chemung, Ontario. An overall seasonal average cutting rate of 0.15 ha/hour was achieved (Wile and Hitchin, 1977). Based on a seasonal estimate of 400 to 500 hours of cutting time for the Orangeville Reservoir operation (G. Gespardy, Pers. Comm.), a total of 60 to 75 ha per season could be cut. This is roughly equivalent to a complete cutting of the western arm of the Orangeville Reservoir. Harvesting removes approximately 80% of the above-ground biomass (Table 4). If it is assumed that the western arm of the reservoir contains 50% of the total biomass, then harvesting would remove a total of 2.01×10^5 kg dry weight of biomass, or 420 kg TP and 4,200 kg TN. These weights are equivalent to 40% of the nutrients contained in the aquatic vegetation.

DISCUSSION

In assessing the feasibility of mechanical weed harvesting as a method of nutrient management it is necessary to determine both the efficiency of biomass removal and the net removal of nutrients by the vegetation. Harvesting efficiency depends on biomass, regrowth rates and methods of reproduction of the dominant plant species. In determining the potential for improvement in water quality, it is necessary to identify the major nutrient sources to the vegetation and the potential for release of nutrients by the vegetation after die-off.

Harvesting Efficiency

Historical records of the effects of mechanical harvesting on water milfoil have produced conflicting results. Mechanical harvesting of Eurasian water milfoil from Chemung Lake in Ontario were shown to reduce stem densities (Wile and Hitchin, 1977). Similarily, Bryant (1970) demonstrated that Eurasian water milfoil regrowth was retarded after harvesting. Research on American water milfoil, likewise indicated an initial

TABLE 5: BIOMASS REMOVED VIA MECHANICAL PLANT HARVESTING DURING 1984

Total biomass = Number of harvester loads x wet weight x moisture content

= $\underset{\text{loads}}{470} \times 1{,}000 \ \frac{\text{lbs}}{\text{load}} \times 91.30\%$ moisture

= 1.85×10^4 kg

Total P removed = 1.85×10^4 kg $\times$ 0.21% P

= 39 kg

Total N removed = 1.85×10^4 kg $\times$ 2.09% N

= 390 kg

---

reduction in density and a reduced rate of regrowth (less than 20 cm per month) (Seinwill, 1968). In multi-year studies, Kimbel and Carpenter (1979) found that even one harvest per year reduced Eurasian water milfoil production the following year. Most authors do agree, however, that more than one harvest per season is needed to control water milfoil regrowth (i.e., Nichols, 1974; Wile and Hitchin, 1977). Kimbel and Carpenter (1979) found multiple harvests to be more effective than single harvests in reducing the amount of regrowth within a growing season and that recovery from a single harvest declines as the date of harvesting becomes progressively later in the season. This pattern correlates with declining water milfoil productivity in the late summer and early fall (Forsberg, 1959; Adams and McCracken, 1974). On the other hand, research in Brititsh Columbia (Anon, 1981) indicated that harvesting may actually stimulate water milfoil growth by removing the shading plant canopy, allowing greater light penetration to the basal shoots.

Results of the 1984 Orangeville cutting operation are too preliminary to draw meaningful conclusions. However, it should be noted that a single cutting reduced biomass in cutover areas by an average of 80%.

Water Quality Improvement

The use of mechanical harvesting to control nutrient concentrations in water has been shown to be effective for certain plant species such as water hyacinth which obtain nutrients largely from the water column (Steward, 1970; Sheffield, 1967) . However, in general, the application of this technique to Eurasian water milfoil has not been effective in reducing the nutrient content of a water body unless concentrations are very high, e.g., 0.5 ug/mL (Bole and Allan, 1978).

Studies on nutrient uptake in both water milfoil species have generally indicated similar uptake patterns. Roots, as well as shoots, are capable of taking up and translocating nitrogen, phosphorus, and other nutrients in significant amounts. The ability of water milfoil to takeup essential nutrients from whichever source is most available, is a significant ecological advantage.

While lakes exhibiting dense growths of Myriophyllum spicatum usually have water-borne phosphorus levels in excess of 0.02 mg/L (Forsberg, 1964), studies have indicated that when water milfoil is rooted, as is the case in the Orangeville Reservoir, phosphorus nutrition is independent of water concentration (Wilson, 1972; Bole and Allan, 1978). Root uptake of phosphorus (Mulligan and Baranowski, 1969; Bristow, 1975) has also been demonstrated in American water milfoil.

Based on the results of the nutrient input-output budget for Orangeville Reservoir, it appears that little phosphorus is removed from the water column by plant uptake. Organic muck bottom sediments such as those found in the reservoir have been shown to provide an ideal nutrient source for both American and Eurasian water milfoil (Sculthorpe, 1967). While average total phosphorus concentrations in the water column are relatively high in the Orangeville Reservoir (up to 0.056 mg/L), phosphate phosphorus concentrations are significantly lower, accounting for only 14% of the total phosphorus loading on an annual basis (Figure 2). Thus, under these conditions the sediments represent a more favourable nutrient source.

The potential for nitrogen control through plant removal appears significantly higher. Based on the input-output budget, approximately 53% or 9,500 kg of the TN entering the reservoir is retained. Of this amount approximately 7,000 kg is in the form of nitrate. According to biomass calculations, the nitrate retained by the reservoir could account for approximately 67% of the TN contained in the plants. The importance of this mechanism of plant uptake is corroborated by the depletion of nitrate and ammonia from the water column during the growing season, despite the fact that atmospheric and inflow loadings are highest during this period of the year. Aquatic macrophytes also appear to introduce significant quantities of nitrogen into the water column through die-off, as indicated by increasing concentrations of inorganic nitrogen forms in the reservoir outflow during the fall and winter. Outflow loading data indicate that approximately 2,400 kg, or 80% of the total nitrate load from the reservoir to the Credit River occurs between November and April.

Nitrogen is recognized as a significant contributor to eutrophication in the upper Credit River. Based on an assimilative capacity study, the MOE (1980) suggests that nitrogen is the limiting nutrient in the system. The Town of Orangeville has similarly recognized nitrogen as a detriment to water quality in the upper Credit River, and has incorporated a denitrification unit into the expansion design of the Water Pollution Control Plant (WPCP).

In the environmental assessment for the WPCP expanison, IEC BEAK (IEC, 1981) calculated that nitrogen loadings from the Orangeville Reservoir and the WPCP accounted for 85-90% of the total nitrogen loading to the Credit River, measured at the Highway 10 crossing. Approximately 20% of the total loading was directly attributed to Orangeville Reservoir outflow. With the commencement of operation of the denitrification unit in the spring of 1985, it is anticipated that 85% of the nitrogen in the WPCP effluent will be removed. It has been calculated in this report that approximately 50% of the nitrogen in the Reservoir outflow could be permanently removed via plant harvesting. Thus the total nitrogen loading to the Upper Credit from these two sources could potentially be reduced by up to 65%.

An improvement in the dissolved oxygen regime of the reservoir may also be achieved as a result of harvesting. Fisheries studies conducted in the reservoir attribute critical oxygen deficiencies observed in both late summer and winter, to plant growth (nocturnal oxygen demand) and winter die-off (oxidation), respectively (McCartney and Fullard, 1973; McCartney, 1974; Hogg, 1975).

CONCLUSIONS AND RECOMMENDATIONS

It is recognized that the results of this study may be subject to large errors as a result of assumptions and inadequate data. Nonetheless, a number of interesting points are raised which might have practical implications for reservoir management in southern Ontario. Based on a simplified input-output budget for total phosphorus and total nitrogen, the Orangeville Reservoir was found to act as a nutrient sink rather than a source to downstream waters. The major storage compartment for both nitrogen and phosphorus is the highly organic sediments. However, aquatic vegetation contains significant amounts of potentially bioavailable nutrients. Net phosphorus retention by aquatic vegetation was small, and it is unlikely that plant harvesting will significantly improve phosphorus concentrations in the water. This condition is attributed to the fact that most of the phosphorus used by plants is obtained via the sediments. There is no indication of phosphorus release during winter die-off, suggesting that phosphorus tied up in the plants is returned to the sediments, thus completing the internal cycle.

On the other hand, about 67% of total nitrogen requirements by plants may be obtained from the water column. Thus harvesting represents a potentially effective method of nitrogen control. The need for nitrogen control in the upper Credit River has been recognized by both MOE and the Town of Orangeville in the incorporation of a denitrification unit in the Orangeville Water Pollution Control Plant.

Based on these conclusions it is recommended that the monitoring program be expanded and continued through at least one full growing season. This monitoring should include more extensive measurements of nutrient inputs. This recommendations was accepted by the Research Advisory Council of the MOE. One year of nutrient input and output measurements are being carried out on the Orangeville Reservoir in 1986.

REFERENCES

Adams, M.S. and M.D. McCracken. 1974. Seasonal production of the Myriophyllum component of the littoral zone of Lake Wingra, Wisconsin. J. Ecol. 62:457-465.

Anon. 1981. A summary of biological research on Eurasian milfoil in British Columbia. Vol. XI: Inf. Bull. Aquat. Plant. Manage. Program, B.C. Ministry of the Environment.

Atmospheric Environment Service (AES). 1982. Canadian Climate Normals. Vol. 3: Precipitation 1951-1980. Environment Canada, 602 p.

Bole, J.B. and J.R. Allan. 1978. Uptake of phosphorus from sediment or by aquatic plants, Myriophyllum spicatum and Hydrilla verticillata. Water Res. 12:353-358.

Bristow, J.M. 1975. The structure and funtion of roots in aquatic vascular plants, pp. 221-236. IN: J.G. Torrey and D. Clarkson (eds.), The Development and Function of Roots. Acad. Press, N.Y.

Bryant, C.B. 1970. Aquatic weed harvesting - Effects and Costs. Hyacinth Control J. 8(2):37-39.

Chan, W.H., A.T.J.S. Tang and M.A. Lusis. 1983. Precipitation concentration and wet deposition fields of pollutants in Ontario, September 1980 to December 1981. Air Resources Branch, Ontario Ministry of the Environment, 79 p.

Forsberg, C. 1964. The vegetation changes in Lake Takern, Sweden. Bot. Tidsk. 58:44-54.

Forsberg, C. 1959. Quantitative sampling of subaquatic vegetation Crikos 10:233-240.

Grace, J.B. and L.J. Tilly. 1976. Distribution and abundance of submerged macrophytes, including Myriophyllum spicatum in a reactor cooling reservoir. Arch. Hydrobiol. 77:475-487.

Hogg, D.M. 1975. Orangeville Reservoir Creek Census. OMNR, 7 p.

IEC Consultants Ltd. (IEC). 1981. Environmental Assessment Report for Water Pollution Control Plant Expansion. Town of Orangeville.

Kimbel, J.C. and S.R. Carpenter. 1979. The dynamics of Myriophyllum spicatum biomass following harvesting. IN: J.E. Breck, R.T. Prentki and O.L. Loucks (eds.) Aquatic Plants, Lake Management and Ecosystem Consequences of Lake harvesting. Inst. Enviro. Studies. Univ. Wisconsin.

M.M. Dillon Ltd. 1966. Orangeville Dam Project: Preliminary Engineering Report. Prepared for the Credit Valley Conservation Authority, 32 p.

McCartney, M.J. 1974. Sex and the single trout or spawning beds at Orangeville Reservoir for speckled and rainbow trout. Prepared for the Credit Valley Conservation Authority, 4 p.

McCartney, M.J. and J.H. Fulland. 1973. The Orangeville Reservoir: An Ecological Study. Prepared for the Credit Valley Conservation Authority, 168 p.

Mulligan, H.F. and A. Baranowski. 1969. Growth of phytoplankton and vascular aquatic plants at different nutrient levels. Verh. Int. Ver. Limnol. 17:802-810.

Nichols, S.A. 1974. Mechanical and Habitat Manipulation for Aquatic Plant Management. Wisconsin Dept. Nat. Res. Tech. Bull. No. 77, Madison, Wisconsin, 34 p.

Ontario Ministry of the Environment (MOE). 1975. Outlines of Analytical Methods. Laboratory Services Branch, Technical Report, 94 p.

Sculthorpe, C.D. 1967. The Biology of Aquatic Vascular Plants. Edward Arnold, London, 610 p.

Seinwill, G.D. 1968. Mechanical Harvesting of Lake Weeds. Univ. Industry Res. Newsl., Univ. of Wisconsin, 3(3):16-17.

Sheffield, D. 1967. IN: D.S. Mitchell (ed.). 1974. Aquatic vegetation and its use and control, UNESCO, Paris.

Steward, K.K. 1970. Nutrient removal potentials of various aquatic plants. Hyacinth Control J. 8(2):34-35.

Taub, F.B. (ed.) 1984. Lakes and Reservoirs. Ecosystems of the World, No. 23. Elsevier, Amsterdam, 643 p.

Water Survey of Canada. 1983. Historical Streamflow Summary. Ontario - to 1982. Inland Waters Directorate, Environment Canada, Ottawa, 520 p.

Wile, I. and G. Hitchin. 1977. An Assessment of the Practical and Environmental Implications of Mechanical Harvesting of Aquatic Vegetation in Southern Chemung Lake. Ontario Ministry of the Environment and Ministry of Natural Resources, 180 p.

Wilson, D.O. 1972. Phosphate nutrition of the aquatic angiosperm, *Myriophyllum excalbescens*. Limnol. and Oceangr. 17(4).

TWO BIOASSAYS FOR THE RAPID DETERMINATION OF THE EFFECTS OF DREDGED MATERIAL DISPOSAL ON PRIMARY PRODUCTION AND PHOSPHORUS KINETICS IN OPEN WATERS.

Calum N. Ewing and C. Nalewajko

Life Sciences Division, Scarborough Campus,
Univercity of Toronto, Toronto, Ontario, M1C 1A4.

ABSTRACT:

The open water disposal of dredged lake sediments can have potential toxic effects on the primary production in the receiving waters. In addition, the availability of nutrients and their cycling can be greatly affected. To date studies of dredgeate toxicity have examined only the effects on photosynthesis and have used only the sediment elutriates to assess toxicity. We now present two bioassays that (1) allow the determination of toxic effects of whole sediments on primary production, as opposed to sediment elutriates or extracts, and (2) allow determination of the effects of whole sediments and elutriates on phosphorus cycling.

The effects of Lake Ontario sediments on the primary production and phosphorus kinetics of epilimnetic phytoplankton assemblages were investigated. Sediment toxicity was assessed using sediment elutriates and whole sediments. The effects of both, on primary production, were measured using the incorporation of ^{14}C, into DMSO extractable compounds, over a range of irradiances. Elutriates prepared from polluted sediments (Toronto Harbour) showed only minor toxic effects (24% depression of Pmax) at a 10% (v/v) dosage. Whole sediment depressed the maximal photosynthetic rate (Pmax) by up to 80%.

The effects of sediment disposal on phosphorus cycling were assessed using $^{32}P\text{-}PO_4$ uptake kinetics. Phosphate turnover time was found to increase with elutriate addition. The addition of whole sediment caused small but not significant decreases in turnover time.

The observed effects are best explained by the high concentrations of phosphorus and toxic chemicals that are present in the sediments but not extracted during the elutriation process. The high concentration of bacteria in the sediment and the physicochemical properties of sediments

may play an important role. These bioassays can be used to rapidly assess the potential toxic effects of dredged sediments, before disposal in open water.

INTRODUCTION:

The harbours of Lake Ontario have been dredged for navigation since the late 19th century. These harbour sediments contain extremely high concentrations of metals and other contaminants (Nriagu et al. 1983). Since open water disposal is the cheapest method (Iskandar et al., 1984), it has been the preferred way to dispose of contaminated sediments. Recent calculations show that the disposal of this dredged material contributes approximately 400000 metric tons per year of fine sediment to the sediment budget of Lake Ontario (Kemp and Harper, 1976).

Of major concern in the dumping of contaminated sediments is the potential for release of metals and other toxins and their effects on the lake biota at the dump site. The metals released and their concentrations depend on the chemical speciation and the physical conditions experienced during release (Mudroch and Davies, 1985). Metals tend to be associated with clay (<4μm) and silt (<63μm) sized particles (Mudroch, 1983) and these, especially the clay sized fraction, stay suspended the longest after dredging or dumping (Iskandar, et al., 1984).

Many metals are released during dredging or dumping operations (see for example Tramontano and Bohlen, 1984; Iskandar et al., 1984). A second effect of the dumping of sediments in open water is the alteration of the nutrient chemistry of the receiving water, especially with respect to phosphorus. Under aerobic conditions, such as those in the epilimnion of receiving waters, sediments tend to act as sinks for phosphate (Mortimer, 1971). However, Twinch and Peters (1984) showed that oxidized sediments can act as a source of phosphate if the phosphate concentration in the water is very low, as might occur as a result of biotic utilization.

The USEPA and Corps of Engineers developed the technique of sediment elutriation to simulate the release of sediment associated contaminants from dumped dreadgeates (see Mudroch and Davies, 1985). Few studies to date have looked directly at the effects of sediment contaminants or sediment disposal on primary producers (see Flint and Lorefice, 1978; Munawar et al., 1983; Mayfield and Munawar, 1983). Only one study to date (Young et al., 1985) has looked at the release of algal available phosphate from suspended lake sediments.

Since the technique of sediment elutriation involves extracting contaminants from sediments with water and then separation of the sediment and water, the true effects of exposure of algae to sediments may not be seen as all of the contaminants may not be extracted. In addition, intimate contact between the sediment particles and algal cells is prevented. In view of these reservations, we developed two bioassays, presented here, that directly assess the effects of sediment-associated contaminants on primary production and phosphorus kinetics. Both bioassays are based on the principle of directly exposing the algal cells to sediment particles and measuring the uptake of radio-isotope tracers in the presence of sediment.

The few studies of toxicity of metals and other sediment contaminants suffer from a serious drawback arising from the use of only one light intensity for experiments on photosynthesis and growth (see Munawar et al., 1983; Wong et al., 1982; Wong et al., 1985). This is inadequate for two reasons. Firstly, the effects of metals and other toxins, on photosynthesis and growth, may differ depending on the light conditions experienced by the phytoplankton.. Secondly, the photosynthetic rate at a single light intensity does not yield an accurate estimate of growth rate. The calculation of the light saturated photosynthetic rate (Pmax), and Assimilation number is calculated as the rate of carbon fixation at Pmax per unit chlorophyll a (Platt and Jassby, 1976) and is widely used to indirectly estimate phytoplankton growth rates (Cote and Platt, 1983).

METHODS:

Experimental Design and Sample Collection:

The effects of additions of elutriates and whole sediments on phytoplankton were investigated using natural assemblages from Lake Ontario. Time courses of photosynthesis and phosphate uptake were performed and the response of the photosynthesis vs. irradiance (P-I) relationship to these additions was examined. In all experiments, a correction was applied for the effect of dilution of the algae by the elutriate or sediment addition was corrected for by diluting the control bottles to the same degree with 0.2µm (Nuclepore) filtered lakewater (FLW). All additions of FLW or elutriates were done at a 10% (v/v) dosage. Sediment addition was done at a 2% (v/v) dosage as this is the amount of sediment in a 10% elutriate dosage. All experiments were run at the ambient lake temperature.

Sediment samples were collected from Toronto Harbour (Stn 1354) at Queen's Quay, using a Ponar grab sampler. These samples were placed in polyethylene containers for transport to the laboratory. Water samples were taken from immediately below the surface at an offshore station approximately 2 Km south-west of Toronto Island. These samples were placed in a 25L polyethylene carboy, darkened with black plastic bags, kept cool with ice and transported immediately to the laboratory.

Photosynthesis:

The effects of elutriate and sediment additions on the relationship between photosynthetic rate and irradiance (P-I) were examined. The rate of photosynthesis was measured using the ^{14}C method (Vollenweider, 1969). Filtered lake water, elutriate or sediment were added to 250mL of lakewater in 400mL polycarbonate bottles. These were spiked with 200µl of dilute (20µCi/mL) $^{14}C-NaHCO_3$ (Amersham 2mCi/mL). These bottles were arranged in series in a constant temperature box illuminated from one end with a 500W quartz halogen lamp. Irradiances ranged from less than 3.0 $\times 10^{14}$ to approximately 8 $\times 10^{16}$ quanta $cm^{-2} s^{-1}$. Bottles were incubated for 3-4 hours. All bottles were agitated at approximately 40 minute intervals. Irradiance was measured using a Model QSL-100 quantum meter (Biospherical Instruments Inc.). In bottles with sediment, the irradiance was measured at frequent intervals during the agitation cycle. Irradiance was then plotted against time and the curve was integrated using a Model 620000 planimeter (Keuffel and Esser Co.) to yield the average irradiance in each bottle.

At the end of the incubation, triplicate end-point filtrations of 50 mL were done on glass fibre (GF/C) filters (Whatman Ltd.). Filters were then frozen in glassine envelopes for later analysis. All treatments without sediment were also filtered, in triplicate, on 0.45µm cellulose nitrate membrane (Sartorius Co.) filters. The filters were rinsed with lakewater filtered through GF/C filters, and dissolved in 15mL of PCS scintillation fluor (Amersham) in plastic vials. The radioactivity of the filters was later measured in a Beckman Model LS-6800 scintillation counter. The total amount of radioactivity added was measured in 1.0mL aliquots with 0.2mL of phenethylamine (Kodak Ltd.) added, and PCS as above.

In addition, two series were run to determine the effect of irradiance fluctuation caused by the settling of the sediment in the bottles. These series had 50mL screwcap test tubes glued in the centre of the bottles (Fig. 1). Lakewater (diluted with 10% FLW) was placed inside the tube and spiked with 50 µL of $^{14}C-HCO_3$. In one series lake water was placed in the bottle outside tube and a 2% sediment-water mixture was placed outside the tube in the other series. In this way intimate contact between the phytoplankton and the sediment was prevented but the sediment still caused fluctuation of the irradiance levels. These series were filtered in duplicate (15mL aliquots) onto GF/C filters and frozen as above.

All glass fibre filters were later thawed and the photosynthate was extracted from the cells in 10 mL of dimethyl sulfoxide (DMSO) using the method of Shoaf and Lium (1976) modified by Burnison (1980). DMSO extracts were filtered onto GF/C filters and the filtrate was caught in 15mL plastic scintilation vials. To these vials 5mL of PCS fluor was added and radioactivity was measured as above.

Quench correction curves were calculated with DMSO, chlorophyll and the coloured compounds extracted from the sediments by DMSO.

Phosphate Uptake:

The second bioassay measures the effect of sediment disposal on phosphorus kinetics in phytoplankton. The effects of elutriate and sediment addition on phosphorus uptake was examined in time-course experiments using carrier-free $^{32}PO_4$-P (New England Nuclear Ltd) as a tracer (Lean and Nalewajko, 1976). Lakewater (200 mL) was incubated in the dark in 250 mL Pyrex reagent bottles. Over 1.5 hours, six aliquots were filtered onto both 0.2µm and 1.0µm pore size polycarbonate membrane (Nuclepore Corp.) filters. The 0.2µm pore size filter entraps the entire biotic community while the 1.0µm pore size filter approximates only the phytoplankton fraction. Filters were dissolved in 10 mL of PCS fluor in plastic vials and the radioactivity was measured as above.

Elutriates:

Sediment elutriates were prepared with the method of Mudroch and Davies (1985) from freshly obtained sediments. All filters used were pre-rinsed with 2x15 mL of deionized distilled water. Elutriates were made fresh on the day of experimentation. In the laboratory whole sediment was stored in the dark at 5°C, sealed in plastic bags.

All glassware was soaked for 24 hours in dilute (2%) H_2SO_4 and then rinsed six times with distilled water before use.

Data Analysis:

The photosynthetic data were compared with a Student's t-Test using the points that made up the light saturated portion of the P-I curve.

The phosphate data were compared by analysis of covariance (ANCOVA program Sokal and Rohlf, 1981) and then a Newmann-Kuell's test (Zar, 1974) to determine which treatments were significantly different. All statistics were computed with programs run on an Apple II+ and a DEC PDP-11 computer.

RESULTS:

Photosynthesis:

The results of the photosynthesis - irradiance curve for elutriate addition are shown in Figure 2. The addition of elutriate at a 10% (v/v) dosage had no effect on the initial, light limited part of the curve. However a 24% reduction in the light saturated photosynthetic rate (Pmax) was seen.

This reduction was significant at $P<0.05$.

Figure 3 shows the results of the DMSO extraction of ^{14}C-labelled photosynthate. The control series shows that 60% of all fixed ^{14}C was extracted by the DMSO. The incorporation of ^{14}C into photosynthate, at saturating irradiance levels, was depressed by 29% upon the addition of elutriate and this was significant ($P<0.05$). However the addition of whole sediment caused much greater depression of Pmax (81%). There was no effect on ^{14}C incorporation at light limiting irradiances.

It was important to ascertain whether the depression observed with the addition of whole sediment was due to the fluctuating light caused by the settling of the sediment or to toxic effects of the sediment itself. Figure 3 shows the results of the series run with the phytoplankton physically separated from the sediment. The series with just lakewater outside the test-tubes showed a significant ($P<0.05$) 18% depression of Pmax. The series with sediment outside the tube showed a 29% depression that was also significantly different from control, but not significantly different from the series with lakewater.

Phosphorus Kinetics:

The results of the ^{32}P uptake by the total assemblage ($<0.2\mu m$) and the algal fraction ($\leq 1.0\mu m$) are shown, in Figures 3 and 4 respectively,as the % ^{32}P remaining in the filtrate. When plotted on a natural logarithmic scale the slope of the initial linear portion of the curve approximates the uptake rate constant (k). The reciprocal of this constant is the turnover time of the external phosphate pool. Turnover time is the time required for the algae to take up an amount of phosphate equal to that present. As such, it provides a good indication of the phosphorus status of the population as turnover time has been found to vary inversely with phosphorus demand (Lean and Nalewajko, 1979). The addition of elutriate caused large increases in turnover time in both the total and algal fractions. In both cases these increases were significantly different from control ($P<0.05$). The addition of whole sediment caused very different results. There was an initial very rapid uptake of ^{32}P on the filters and then a return to levels similar to control where a near linear uptake was observed. This initial drop was omitted from the rate calculations. The rate of phosphate uptake upon the addition of whole sediment did not differ significantly from control in either the $>0.2\mu m$ or $>1.0\mu m$ fractions ($P<0.05$). The values for turnover times of all treatments are shown in Table 1.

DISCUSSION:

It has been shown that the addition of elutriates or whole sediment causes decreases in the maximal photosynthetic rate of epilimnetic phytoplankton. This depression was seen in both the total radiocarbon fixation and the amount of ^{14}C incorporated into DMSO extractable photosynthate. The depression was much greater in the treatments with whole sediment than those with elutriate. This great depression of photosynthesis could be expected as a result of the high levels of toxins present in these sediments. The sediments of Stn 1354 are known to be highly contaminated with both metals and organic toxins (MOE, 1985).

Filbin and Hough (1984) showed that DMSO will quantitatively extract labelled photosynthate from plant tissues with a high degree of accuracy. Extraction of this photosynthate allows measurement of the amount of ^{14}C fixed in the presence of whole sediment. The quenching caused by sediment makes direct scintilation counting of filters with sediment impossible while the quenching caused by DMSO in minimal. Thus the effects of exposure to sediments can be measured directly without the use of elutriates.

The lack of significant difference between the series with and without sediment around the test-tubes shows that the observed depression of Pmax is due to the toxic effects of direct exposure of the algae to the sediment and not to the fluctuation in irradiance as the sediment settles.

Phosphorus Kinetics:

The results showed that the addition of elutriate caused significant increases in the turnover time of the external phosphate pool. This would be expected from the large concentrations of phosphate present in sediments and extracted during the elutriation process. An addition of phosphate will increase the phosphate pool and increase the turnover time. Oxidized sediments have been shown to release phosphate and this release seems dependent on the phosphate concentration in the receiving water (Twinch and Peters, 1984). Young et al. (1985) showed that large amounts of algal available phosphate are released from suspended lake sediments.

The rapid initial drop in amounts of ^{32}P remaining in the filtrate in treatments containing whole sediment are likely due to a rapid chemical diffusion of ^{32}P onto the sediment particles. Bacteria attached to the sediment particles may also play an important role in this movement of phosphate. The ^{32}P partitioning between sediment and water quickly reached equilibrium and a linear uptake of ^{32}P by the phytoplankton was seen. While whole sediment may release phosphate it also appears to act as a sink. Overall there was no significant effect on the algal uptake of phosphate. The difference between slowing of phosphate uptake by an increase in the PO_4 pool and by toxic effects of the sediment would seem to be hard to discern. However, if the reduction in phosphate uptake seen on elutriate addition was due to toxic effects, the same or more toxic effect would be expected upon the addition of whole sediment. This was not seen so it can be concluded that the primary effect of exposure to sediments revolves around changes in the external phosphate pool and not poisoning of phosphate uptake mechanisms.

We have presented here two bioassays that permit rapid and direct assessment of the effects of sediment disposal on primary production and phosphorus kinetics. The uptake of ^{14}C, in the presence of whole sediment can be measured by extraction of labelled photosynthate with DMSO. If this is done at a range of irradiance level an accurate picture of the effects on Pmax, and therefore growth, can be achieved. Phosphorus kinetics can be affected by sediment in ways that differ from elutriate addition. This can now be directly assessed using the bioassay presented here.

Acknowledgements:

We wish to thank Dr. R. Boonstra for assistance with the statistical analysis and the field personel of Water Resources Branch, MOE. This work was supported by an MOE Grant to C. Nalewajko.

REFERENCES:

Burnison B.K. (1980) Modified dimethyl sulfoxide (DMSO) extraction for chlorrophyll analysis of phytoplankton. Can. J. Fish. Aqua. Sci. 37:729-733.

Cote B. & T. Platt (1983) Day to day variations in the spring-summer photosynthetic parameters of coastal marine phytoplankton. Limnol. & Oceanogr. 28:320-344.

Filbin G.J. & R.A. Hough (1984) Extraction of ^{14}C-labeled photosynthate from aquatic plants with dimethtl sulfoxide (DMSO). Limnol. & Oceanogr. 29:426-428.

Flint R.W. & G.J. Lorefice (1978) Elutriate-primary productivity bioassays of dredge spoil disposal in Lake Erie. Water Res. Res. 14:1159-1163.

Iskandar I.K., J.H. Cragin, L.V. Parker & T.F. Jenkins (1984) Impact of dredging on water quality at Kewaunee Harbour, Wisconsin. US Army Corps of Engineers, Cold Regions Research & Engineering Laboratory. Report 84-21.

Kemp A.L. & N.S. Harper (1976) Sedimentation rates and a sediment budget for Lake Ontario. J. Great Lakes Res. 2:324-340.

Lean D.R.S. & C. Nalewajko (1976) Phosphate exchange and organic phosphorus excretion by freshwater algae. J. Fish. Res. Bd. 33:1312-1323

--- & --- (1979) Phosphorus turnover time and phosphorus demand in large and small lakes. Arch. Hydrobiol. Beih. 13:120-132.

Mayfield C.I. & M. Munawar (1983) Preliminary study of the effects of contaminants from sediments on algal membranes. J. Great Lakes Res. 9:314-316.

MOE (1985) Historical development and quality of the Toronto Waterfront sediments - Part 1. Ministry of the Environment. May, 1985.

Mortimer C.H. (1971) Chemical exchanges between sediments and water in the Great Lakes - speculations on probable reguulatory mechanisms. Limnol. & Oceanogr. 16:387-404.

Mudroch A. (1983) Distribution of major elements and metals in seddiment cores from the western basin of Lake Ontario. J. Great Lakes Res. 9:125-133.

--- & S. Davies (1984) Chemical speciation of metals in sediment elutriates. Environ. Internat. (in press).

Munawar M., A. Mudroch, I.F. Munawar & R.L. Thomas (1983) The impact of sediment associated contaminants from the Niagara River mouth on various size assemblages of phytoplankkton J. Great Lakes Res. 9:303-313.

Nriagu J.O., H.K.T. Wong & W.J. Snodgrass (1983) Historical records of metal pollution in sediments of Toronto and Hamilton Harbours. J. Great Lakes Res. 9:365-373.

Platt T. & A.D. Jassby (1976) The relationship between photosynthesis and light for natural assemblages of coastal marine phytoplankton. J. Phycol. 12:421-430.

Shoaf W.T. & B.W. Lium (1976) Improved exrtaction of chlorophyll a and b from algae using dimethyl sulfoxide. Limnol. & Oceanogr. 21:926-928.

Sokal R.R. & F.J. Rohlf (1981) Biometry 2nd Ed. W.H. Freeman & Co. San Francisco.

Tramontano J.M. & W.F. Bohlen (1984) The nutrient and trace metal geochemistry of a dredge plume. Estuarine, Coastal & Shelf Science 18:385-401.

Twinch A.J. & R.H. Peters (1984) Phosphate exchange between littoral sediments and overlying water in an oligotrophic north-temperate Lake. Can. J. Fish. Aqua. Sci. 41:1609-1617.

Vollenweider R.A. (1969) A manual on methods for measuring primary productivity in aquatic environments. IBP Handbook No. 12 Blackwell Scientific.

Wong P.T.S., Y.K. Chau & D. Patel (1982) Physiological and biochemical responses of several freshwater algae to a mixture of metals. Chemosphere 11:367-376.

--- , --- & --- (1985) The use of algal batch and continuous culture techniques in metal toxicity study. Adv. Environ. Sci. Tecchnol. (in press).

Young T.C., J.V. De Pinto, S.C. Martin & J.S. Bonner (1985) Algal-available particulate phosphorus in the Great Lakes Basin. J. Great Lakes Res. 11:434-446.

Zar J.H. (1981) Biostatistical Analysis. Prentice Hall.

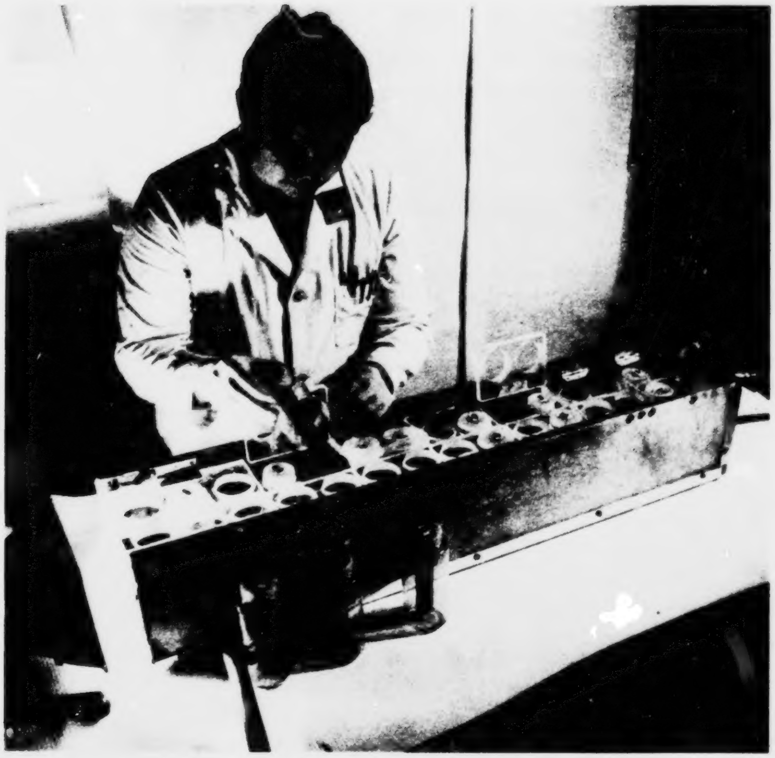
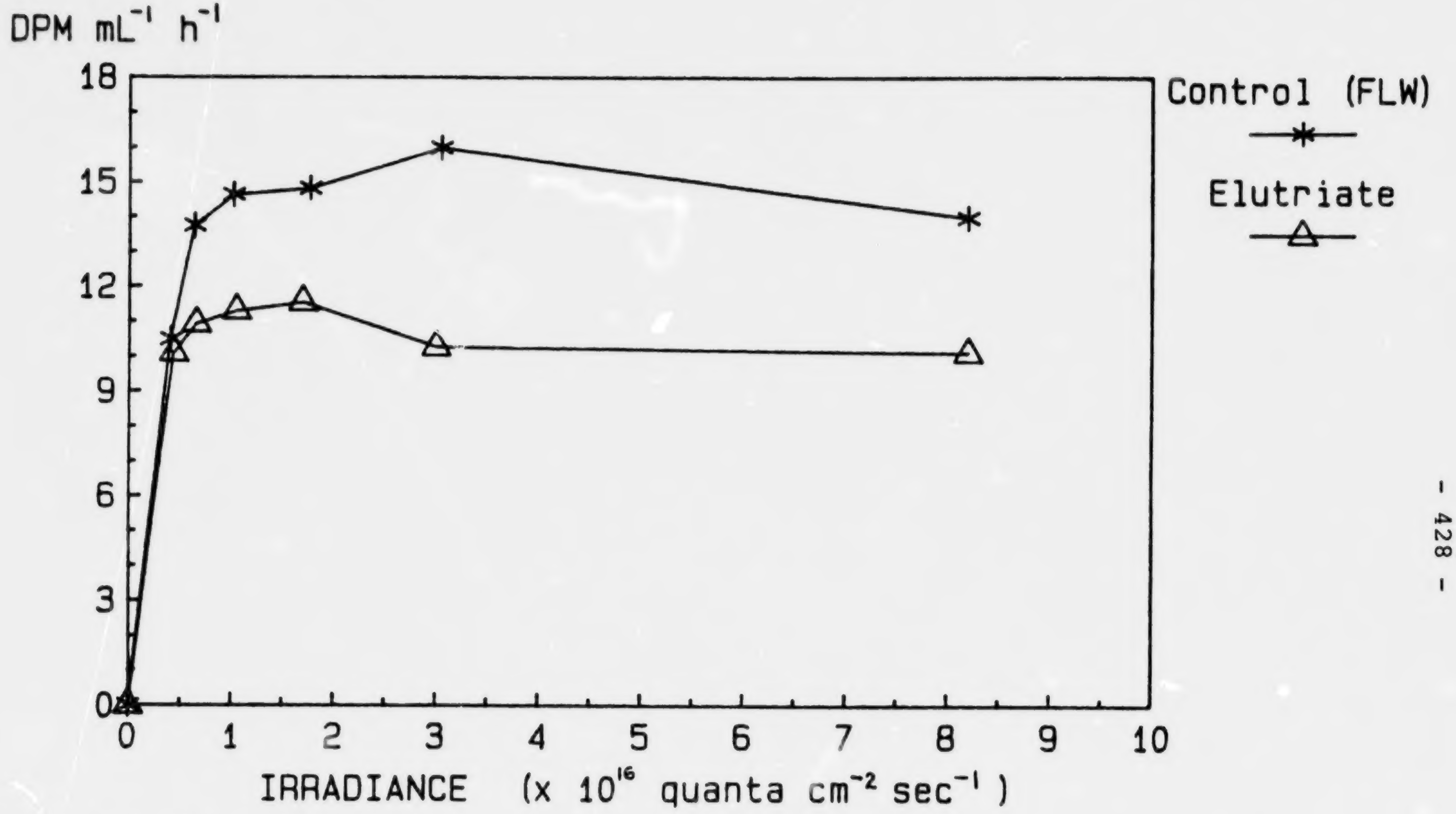


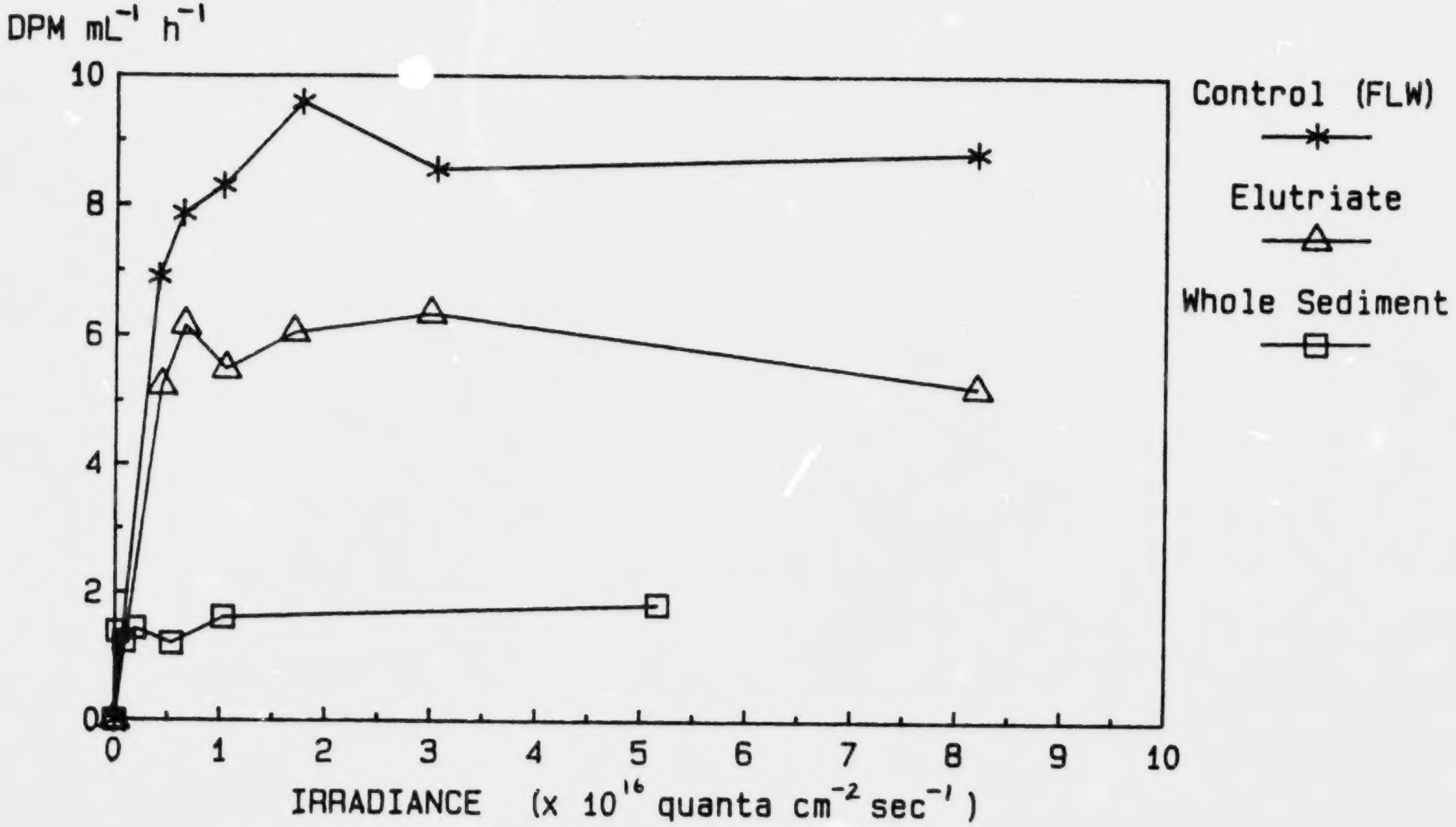
Figure 1: Constant temperature light gradient box used in P-I experiments. Experimental bottles with central test-tube (black) shown at front.

Figure 2: Photosynthesis - irradiance curve of Lake Ontario phytoplankton exposed to Stn 1354 sediment elutriate (10% v/v).



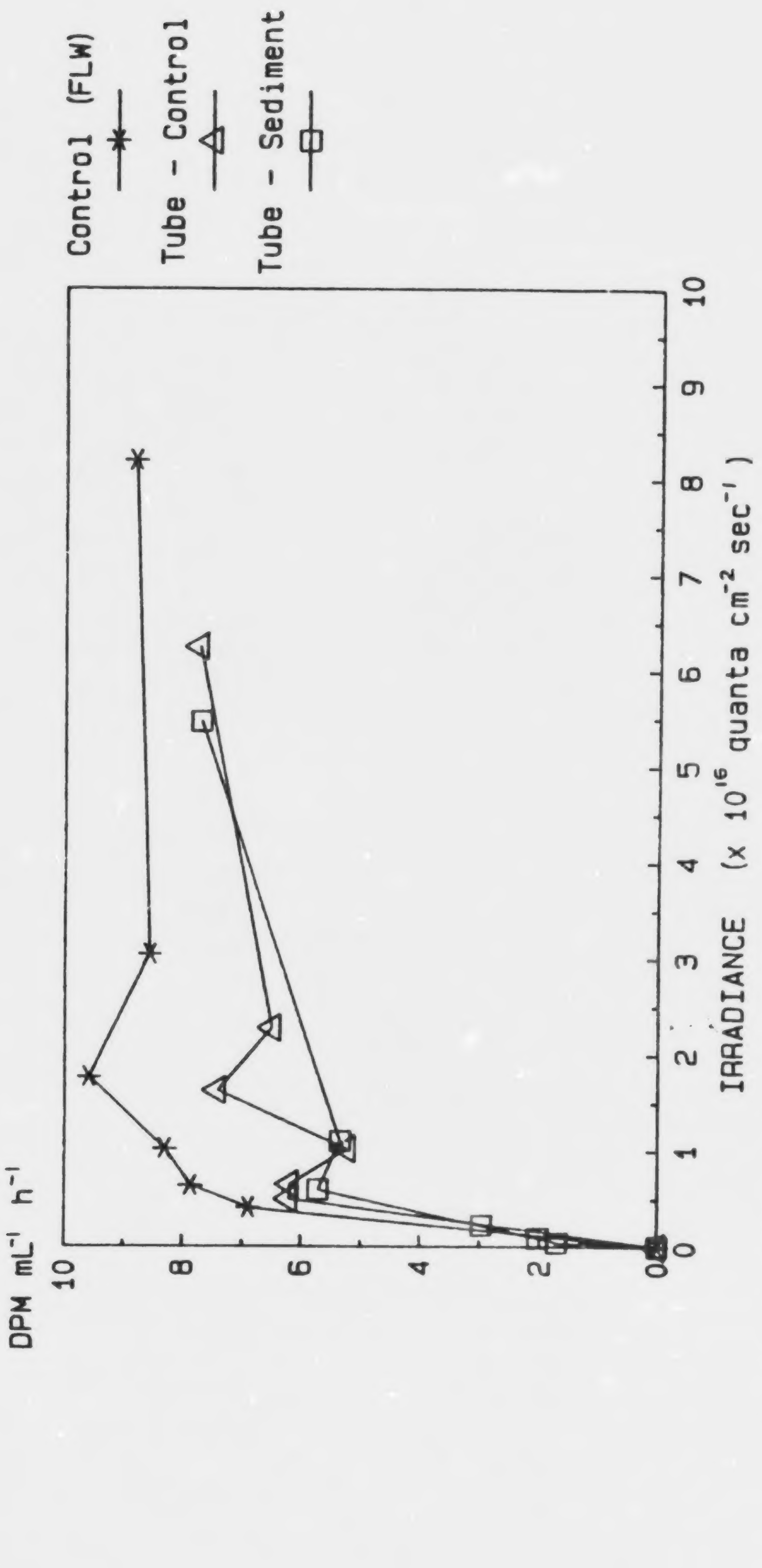
Filtered on 0.45μm Sartorius

Figure 3: Photosynthesis - irradiance curve of ^{14}C-labelled photosynthate extracted in DMSO from Lake Ontario phytoplankton exposed to Stn 1354 sediment elutriate (10% v/v) and whole sediment (2% v/v).



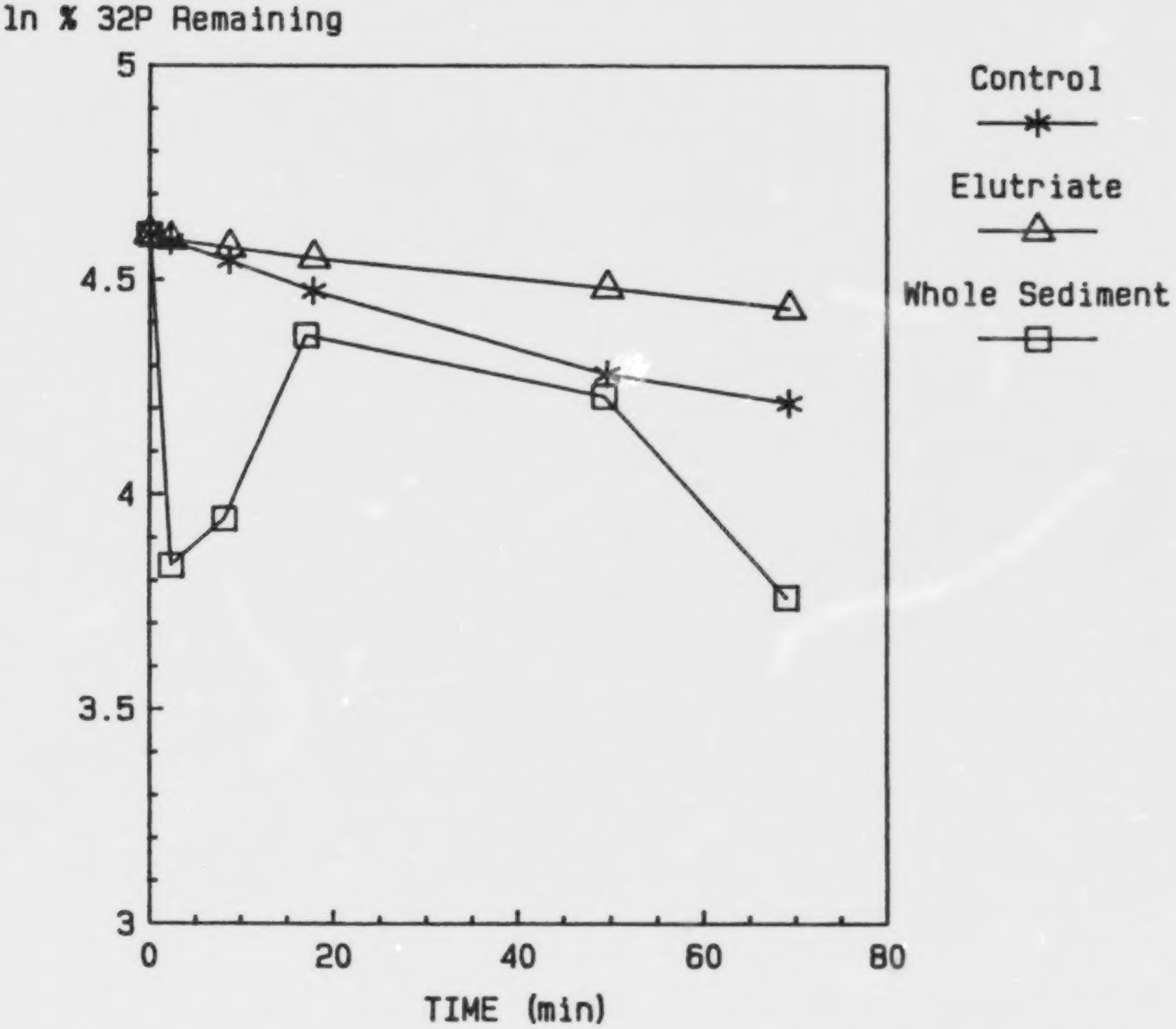
Filtered on Wattman GF/C

Figure 4: Photosynthesis - irradiance curve of ^{14}C-labelled photosynthate extracted in DMSO from Lake Ontario phytoplankton incubated in test-tubes shielded with lakewater or 2% (v/v) sediment in lakewater.



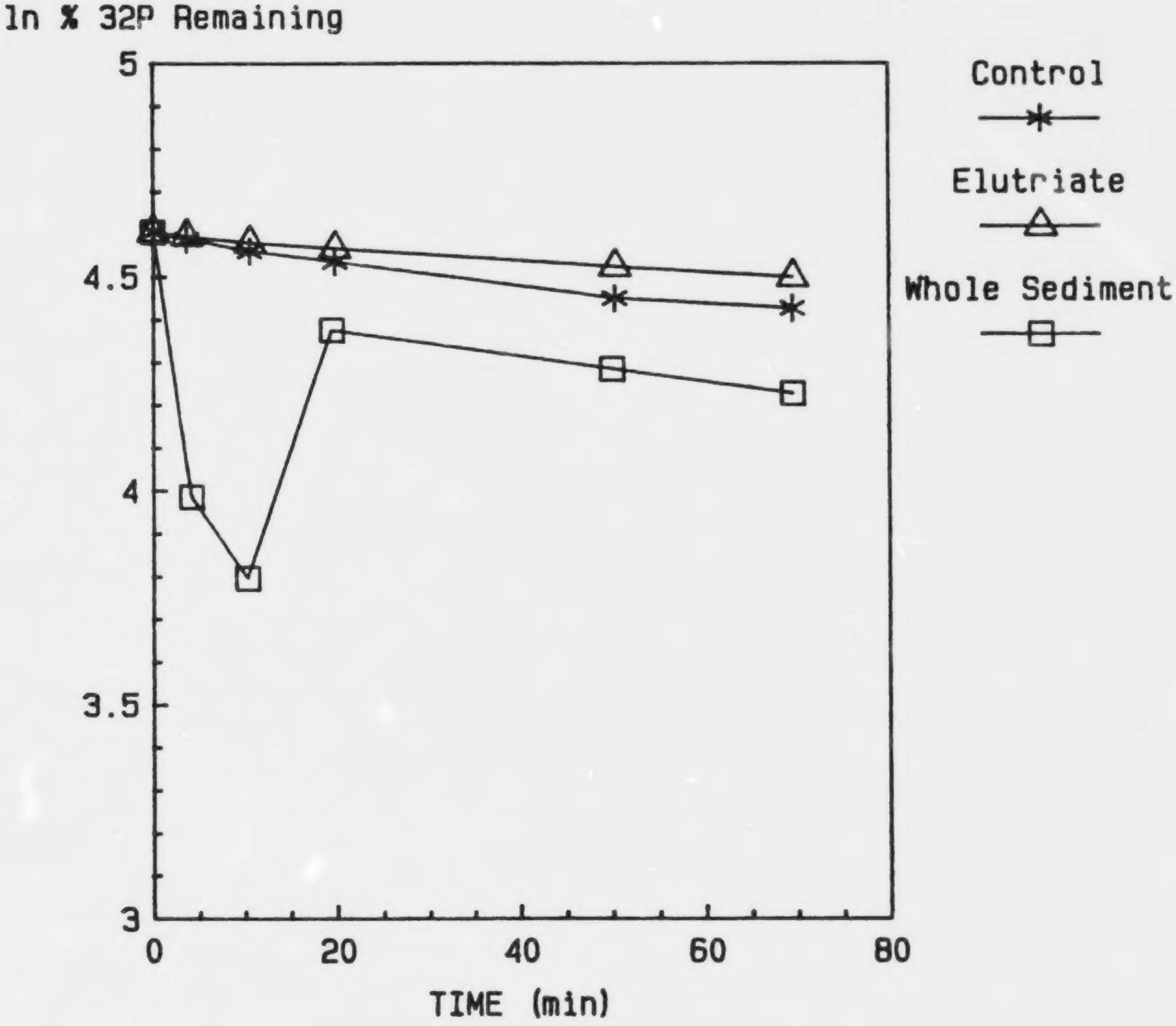
Filtered on Wattman GF/C

Figure 5: Time course of ^{32}P uptake by total assemblage of Lake Ontario biota (>0.2μm) exposed to Stn 1354 sediment and sediment elutriate.



Filtered on 0.2µm Nuclepore

Figure 6: Time course of ^{32}P uptake by Lake Ontario phytoplankton (>1.0µm) exposed to Stn 1354 sediment and sediment elutriate.



Filtered on 1.0µm Nuclepore

Table 1: Turnover times of ^{32}P uptake by Lake Ontario phytoplankton assemblages (Total and >1.0μm).

Treatment	Turnover time (min) >0.2μm	>1.0μm
Control	152	330
Elutriate	414 *	634 *
Whole Sediment	138	336

'*' denotes significant difference from control at $p<0.05$.

PROBABILITY AND STOCHASTIC MODELING OF WATER QUALITY PARAMETERS IN THE THAMES RIVER

V.A. Graham

Research Scientist
Department of Systems Design Engineering
University of Waterloo
Waterloo, Ontario, Canada.

T.E. Unny

Professor
Department of Civil Engineering
University of Waterloo
Waterloo, Ontario, Canada.

L. Logan

Chief, Hydrology Unit
Water Resources Branch
Ministry of the Environment
Toronto, Ontario, M4V 1P5

ABSTRACT

Models for the probability and stochastic behaviour of phosphorous and suspended sediment concentrations in the Thames river have been developed. The historic record of water quality parameters was observed to exhibit a strong non-Gaussian character, and to vary appreciably, depending on the month. Monthly probability distributions for these water quality parameters were described using a five parameter polynomial expression. This model will preserve the mean, variance, skewness, and kurtosis of monthly data. Owing to the non-Gaussian and varying nature of the monthly probability distributions, stochastic models were developed after transforming the data to a set representable by a single Gaussian distribution with constant statistics for all months. The novel transformation will allow almost all the statistical characteristics of the historic sequence to be preserved, since it incorporates the exact monthly probability distribution model of the historic sequence. Application of the ARIMA process to the transformed random variables reveal that an ARIMA[1,1,0] process is appropriate for transformed phosphorous data, and a white noise process for the transformed suspended sediment data.

INTRODUCTION

Quantifying the variations in water quality parameters is essential for developing water quality policy for reducing costly risk to the environment, due to stream-flow degradation. Presently, policy analysts and management are forced to rely on the use of historic records during the formation of policy guidelines, and in monitoring, regulating, and managing the concentration of toxic contaminants in Ontario streams. This approach involves the analyses of records of measured data in determining failure of established water quality criteria. Because water quality data are not deterministic, but random, the objective decision-making can become complicated.

The use of historic records in the work of monitoring and managing water quality is restrictive, in that only a small amount of useful information can be easily extracted. Management is generally limited to simple statistical indicators such as mean and standard deviation of water quality parameters over a period of time. Thus it is not possible to arrive at valuable information on the probability of events or the possibility that a given condition (for example, failure of water quality policy) will persist into future months. The formation of policy criteria for monotoring and managing water quality, however, does not necessarily demand that historic data be used. In fact, mathematical models which incorporate the salient probability feature of the historic record may be used to generate synthetic water quality data. By careful analysis of historical records it is possible to extract useful information on the character of the underlying probability distributions and the probability that a given condition may affect future events (ie. serial relationship between events), and imbed them into mathematical models.

These mathematical models for stream water quality, will allow for a flexible approach to evaluating policy failure; and make the assessing of risk to the environment accurate. They may also be used to provide an abundance of synthetic water quality data to be used in the evaluation of various management scenarios for improving water quality. And would enable projections of the water quality characteristics to be established, when the water system is subjected to a known intervention. Because of the lack of reliable data (without missing values) such an evaluation is currently not possible.

These mathematical models form the subject of this paper. The development of models to characterize water quality uncertainties require rigorous analysis of the statistical and stochastic behaviour of water contaminant parameters. Statistical studies are needed to establish trends, moments, and probability distributions. Stochastic studies will allow the further information on the autocorrelation of successive events to be incorporated. This results of this research will provide a tool that will allow for greater objectivity in the decision making process, and a new approach, based on probabilities, to respond to failure of established water quality policy.

STATISTICAL BEHAVIOUR OF WATER QUALITY PARAMETERS

Models for water quality parameters will be constructed after detailed analysis of actual measured data. In the following the data set to be employed will be briefly described. Water quality data are collected by the Ontario Ministry of the Environment for a number of Canadian locations. These measurements generally include the average monthly concentration of water contaminants. Statistical and stochastic analysis of phosphorous concentration (P_c), and suspended sediments concentration (S_c) will be performed. Data, measured over a considerable time period (up to twenty years) is available. Unfortunately, the available data has a significant number of missing values. This loss of information may not hinder the model development work, but renders the use of pre-programmed computer codes (such as IMSL codes) useless; and requires greater care in extracting the relevant information for probability and stochastic modeling from contigeous data zones. Models will be constructed using data from the Thames rivers. Monthly record, collected over a period of twenty years will be used.

Statistical Analysis of P_c, and S_c

Any stochastic model for the water quality parameters must incorporate the salient statistical features of the historic data itself. Therefore, before model building is attempted, this data will be analyzed to determine its statistical properties. The statistical behaviour of water quality parameter values will be investigated by first studying the character of the principal moments: the mean, variance, skewness, and the excess kurtosis. These statistics are used to provide key information on the character of the underlying probability distribution and to assess closeness of the underlying distributions to Normally distributed random variables (information that is important in constructing stochastic models). Normally distributed random variables are specified by only two statistics, the mean and variance. Higher order moments, such as the skewness and kurtosis, are unique for Normally distributed random variables. In simple language, the skewness (g_1) provides a measure of the degree of symmetry (or lack of symmetry) about the mean. It measures the third central moment and, for a normally distributed random variable is equal to zero. The kurtosis measures the relative 'peakedness' of a distribution. It provides a measure of the fourth central moment and, for normally distributed random variables, is equal to 3. The excess kurtosis g_2 represents values of the fourth central moment greater or less than 3, and as such is zero for Normally distributed random variables. Estimates of the skewness and kurtosis for an arbitrary random variable x is obtained as follows:

$$g_1 = \frac{\frac{1}{N}\sum_{i=1}^{N}[x_i-\bar{x}]^3}{\left(\frac{1}{N}\sum_{i=1}^{N}[x_i-\bar{x}]^2\right)^{3/2}} \qquad g_2 = \frac{\frac{1}{N}\sum_{i=1}^{N}[x_i-\bar{x}]^4}{\left(\frac{1}{N}\sum_{i=1}^{N}[x_i-\bar{x}]^2\right)^{2}} - 3 \qquad 1$$

where N is the total number of x values.

These statistics will be computed using monthly data P_c and S_c occurring over twenty years, for the Thames river. Special care was necessary in computing these statistics, owing to the presence of missing values in the data. Summary statistics of the random variables are presented in the Table 1 and 2.

TABLE 1

STATISTICS FOR MONTHLY PHOSPHOROUS CONCENTRATION P_c
THAMES RIVER

MONTH	MEAN $\bar{P}_c$	STD. DEVIATION σ_P	SKEWNESS $g_{1,P}$	KURTOSIS $g_{2,P}$
Jan	0.357	0.346	2.748	7.458
Feb	0.332	0.253	1.711	1.953
Mar	0.344	0.325	3.241	10.199
Apr	0.249	0.123	1.518	2.777
May	0.316	0.197	0.732	-0.606
Jun	0.599	0.535	0.935	-0.459
Jul	0.452	0.487	1.701	2.202
Aug	0.596	0.594	1.743	2.381
Sep	0.504	0.387	0.685	-0.864
Oct	0.431	0.516	1.989	2.715
Nov	0.352	0.281	1.403	0.867
Dec	0.240	0.179	1.631	2.083

TABLE 2

STATISTICS FOR MONTHLY SEDIMENTS CONCENTRATIONS S_c
THAMES RIVER

MONTH	MEAN $\bar{S}_c$	STD. DEVIATION σ_S	SKEWNESS $g_{1,S}$	KURTOSIS $g_{2,S}$
Jan	8.657	5.559	1.357	1.038
Feb	9.506	4.658	0.124	-1.240
Mar	18.865	16.100	1.765	2.529
Apr	20.031	18.236	3.025	8.523
May	22.193	32.835	3.201	8.556
Jun	17.969	7.614	0.292	-1.065
Jul	19.427	9.308	1.491	1.814
Aug	19.464	8.985	0.182	-1.467
Sep	23.773	12.032	0.971	1.234
Oct	17.147	6.174	-0.019	-1.255
Nov	17.350	8.338	1.778	2.039
Dec	12.484	7.007	0.289	-1.121

The statistics estimated indicate appreciable variation in the monthly mean, $\bar{P}_c$, and $\bar{S}_c$ throughout the year. The monthly standard deviation, skewness, and kurtosis are also observed to change significantly from month-to-month. This variation in moment estimates tells us that the probability distribution of each of these random variables are not the same for all months. If the random variables had a constant distribution for all months, then moments estimates would be the same for all months. Since this is not the case it follows that the probability distributions are changing from month-to-month. Thus a procedure which uses annual means and variance etc. (which implies a fixed probability distribution) in policy decision making, could be very misleading, and could mask serious and persistent violations of policy guidelines for specific seasons in the year.

Accurate stochastic models for the random variables should reproduce much of these statistics, if the models are expected to represent the process. Thus the process itself changes monthly, and hence is nonstationary. This may be so partly because variable such as stream flow, which affects the concentration of water quality parameters, varies seasonally, depending on factors as snow melt or precipitation. Incorporating the probability features of the historic data in stochastic models will require some mathematical description. Developing suitable mathematical representations for the water contaminants is the subject of the following section.

Probability Model for Water Quality Parameters, P_c and S_c

Since the probability distributions of the random variables is found to vary monthly, it is not possible to arrive at a fixed distribution function for all months. In this study probability functions for monthly random variables will be sought. In the development of probability models it is possible to empirically determine frequency functions and fit equations to these curves. However, a more appropriate way is to determine the density function using the moments itself (Frazer, 1976). In this way density functions are guaranteed to reproduce the key moments of the historic data.

If $P[x]$ denote the true density of random variable x, (The variable x is used to represent any one of P_c, and S_c.) and $p(x)$ used to represent a mathematical approximation of the density function $P[x]$, then $p(x)$ must be chosen to preserve the moments of the unknown $P(x)$ that is important to the problem at hand. In our work probability models are needed to infer cumulative probability estimates of monthly events, and to preserve the principal moments in synthetic water quality data, generated using a developed stochastic model. Thus a simple polynomial representation for the monthly density function may be used. The polynomial density function which exactly reproduces the estimated moments of historic data will be used to represent the data. The approximate polynomial density can be expressed as

$$p[x]=\sum_{i=0}^{n} c_i x^i \qquad 2$$

Our quest is to identify $p(x)$ such that the i^{th} moment is conserved. The coefficients c_i must be so chosen that the sum of squares function $J(c_0,c_1,...c_i)$ is minimized. The sum of squares function is defined as follows:

$$J(c_0,c_1,...c_n)=\int_{x_l}^{x_u} [P(x)-p(x)]^2 dx \qquad 3$$

The coefficients c_i are obtained by solving the system of equations resulting from

$$\frac{\partial J}{\partial c_i}=0 \quad i=0,1,2,... \qquad 4$$

It is desired that the first four moments need be conserved, hence the approximate polynomial density expression will have only five parameters, that is, n=4. Also by noting that

$$\int_{x_l}^{x_u} x^i \, P(x) dx \;=\mu_i \qquad 5$$

where $\mu_o=1$, μ_1 is the mean, and $\bar{x}$ provides an estimate of it; μ_2 is the second moment about the origin, and can be estimated from the variance σ^2; μ_3 and μ_4 are the third and fourth moments about the origin, respectively, and can be estimated from the skewness and kurtosis, respectively. The above set of equations, after substituting for $p(x)$ and integrating, simplify to the following set of system of equations

$$\mathbf{P\,C = M} \tag{6}$$

where

$$P = \begin{bmatrix} p_1 & p_2 & p_3 & p_4 & p_5 \\ p_2 & p_3 & p_4 & p_5 & p_6 \\ p_3 & p_4 & p_5 & p_6 & p_7 \\ p_4 & p_5 & p_6 & p_7 & p_8 \\ p_5 & p_6 & p_7 & p_8 & p_9 \end{bmatrix} \qquad C = \begin{bmatrix} c_0 \\ c_1 \\ c_2 \\ c_3 \\ c_4 \end{bmatrix} \qquad M = \begin{bmatrix} 1 \\ \mu_1 \\ \mu_2 \\ \mu_3 \\ \mu_4 \end{bmatrix} \tag{7}$$

and $p_i = \dfrac{x_u^i - x_l^i}{i}$; μ_2 μ_3, and μ_4 are the second, third, and fourth moments of x about the origin, respectively.

and the coefficients c_i are obtained after inversion:

$$\mathbf{C = P^{-1}M} \tag{8}$$

The moments about the origin can be estimated from the central moments estimated in Tables 1 and 2. Values of x_u and x_l necessary to evaluate integrations involving the polynomial density function were obtained by setting them to the corresponding extremes observed after 20 years.

TABLE 4

TWENTY YEAR EXTREME VALUES
OF TOXIC CONCENTRATION IN THAMES RIVER

Variable	x_u (MG/L)	x_l (MG/L)
Phosphorous	2.353	0.059
Sediments	135.0	2.000

The polynomial model was observed to reproduce the first four moments exactly, and to produce a distribution function with total probability of unity. The model, however, has the difficulty that it does not guarantee a smooth density function, with limited turning points as would exist in practice.

STOCHASTIC MODEL CONSTRUCTION

Stochastic models of the water quality variables, will be addressed by studying the phosphorous and suspended sediment concentrations separately. The series of water quality parameters is a nonstationary series: the series are shown to be governed by different non-Gaussian probability distributions for different months. An accurate stochastic model requires maintaining the salient probability characteristics of historic record; these include maintaining the monthly varying mean, variance, skewness, and kurtosis. This is done most effectively if the monthly marginal distribution is incorporated in the modeling activity. Thus, the principal moments (mean, variance, skewness, kurtosis, and higher order moments) will automatically be preserved in synthetic sets of water quality parameters generated using these models. Owing to this complex nonstationary behaviour of monthly water quality parameters and further because the series are non Gaussian, direct application of the ARIMA process is not appropriate.

Various methods have been suggested in the literature for correcting nonstationary behaviour in stochastic series. The method of differencing is a popular approach. While differencing can correct some forms of nonstationarity, it requires that the original series be Gaussian. Another method for correcting nonstationary behaviour in stochastic series is the method of deseasonalizing the series (eg. Tao and Delleur, 1975, Hipel et al, 1977). This method will produce a series that is stationary in the mean, and having constant variance—that is, having zero mean and unit variance. If these were the only two properties desired to be reproduced in synthetic water quality data, then the deseasonalizing method would be appropriate. But because deseasonalization is a linear transformation, higher order moments of the transformed series will still be varying throughout the year. The use of a power (non-linear) transformation such as the transformation due to Box and Cox (1964) is also quite popular for rendering inherently non-Gaussian series approximately Gaussian; but since the distribution of monthly water quality events changes monthly, a single power transformation would be in appropriate.

Others (eg. Hipel and McLeod, 1979) have suggested applying Fourier analysis to estimate time varying trends in the data, and modeling the resultant series. This approach is useful primarily when there are known cyclic trends imbedded in the series. It is not applicable to the water quality parameters under investigation since the distribution of the detrended set also will be non-Gaussian and time varying.

The popular transformation procedures, namely, differencing, or deseasonalizing may not accurately correct for non-stationarity of monthly water quality parameter, and also render the series representable by a Gaussian distribution. To do this novel methods must be applied. The problem at hand requires transforming the series to a stationary set that is representable by a single Gaussian distribution. This problem can be solved if the random variable were to be transformed into a new random variable that is Gaussian, using the actual probability distributions for the random variable.

Probability Integral Transformation

Before the ARIMA process can be applied it is necessary to correct for the non-Gaussian and monthly varying probability distribution in water quality parameters series. These objectives can be attained if these random variable were to be transformed into a new Gaussian random variable with invariant statistics— with an equal mean and variance, for all months. The transformation functions must be chosen in such a way as to map monthly sets of water quality data from its parent distribution to this new Gaussian domain. But since the distribution for water quality parameters (say x) changes monthly, the transformation must also change monthly. If $x_{t,j}$ denotes a measure of water quality in month j and, $\varsigma_{t,j}$ denote Gaussian variable corresponding to the same month, and f_j denote the monthly transformation function, then

$$f_j[x_{t,j}]=\varsigma_{t,j} \qquad 9$$

For simplicity the mean and variance of the Gaussian distribution for ς will be chosen to be 0 and 1, respectively, for all months. Therefore, the annual set of $\{\varsigma_{t,j}\}$ will be $N[0,1]$.

In this problem the densities of both variables are known, but the transformation functions are unknown. The functional relationship between $\varsigma_{t,j}$ and $x_{t,j}$ requires that the mapping, between the Gaussian distribution and the distribution for $x_{t,j}$, be done in such a way as to ensure that the marginal probability is unaltered. Let $g[\varsigma_{t,j}]$ denote the single marginal Gaussian density function of $\varsigma_{t,j}$, in all months and $P_j[x_{t,j}]$ the monthly density function of $x_{t,j}$. Now, if a new variable $u_{t,j}$ is defined such that it is assigned the cumulative probability of $\varsigma_{t,j}$, then

$$u_{t,j} = \int_{-\infty}^{\varsigma_{t,j}} g(t)dt = \frac{1}{\sqrt{(2\pi)}}\int_{-\infty}^{\varsigma_{t,j}} e^{-\frac{t^2}{2}} dt = \frac{1}{2}\left[1 + erf(\frac{\varsigma_{t,j}}{\sqrt{2}})\right] \qquad 10$$

It can be shown (Blake, 1979) that values of $u_{t,j}$ will be uniformly distributed on the interval (0,1). Also if another variable $v_{t,j}$ is defined such that it is assigned the cumulative probability of $x_{t,j}$, then

$$v_{t,j} = \int_{x_l}^{x_{t,j}} P[x^*_{t,j}]dx^*_{t,j} = F(x_{t,j}) \qquad 11$$

Again it can also be shown that values of $v_{t,j}$ will be uniformly distributed, on the (0,1) interval. (Random variables which are transformed by their distribution function always yield a transformed variable that is uniformly distributed.) Since the random variable $u_{t,j}$ and $v_{t,j}$ are represented by the same distribution, for all time t and for a specific month j, and the sought transformation requires that the cumulative probabilities be maintained, it follows that for the same value of t,j: $u_{t,j}=v_{t,j}$. Hence, integral transformations may be equated to give the desired transformation function f_j for mapping between $\varsigma_{t,j}$ and $x_{t,j}$.

$$\frac{1}{2}\left[1 + erf\frac{\varsigma_{t,j}}{\sqrt{2}}\right] = \int_{x_l}^{x_{t,j}} P[x^*_{t,j}]dx^*_{t,j} = F(x_{t,j}) \qquad 12$$

Hence,

$$\varsigma_{t,j} = f_j[x_{t,j}] = \sqrt{2}erf^{-1}\left[2F(x_{t,j})-1\right] \qquad 13$$

The transformation function is therefore defined by equation 13, and requires only monthly values of c_i to specify the probability density function (eq. 2) for the water quality variable, prior to performing the integration of equation 31. Computation of the inverse error function is discussed in Strecok (1968).

Therefore the transformation function can be computed by first computing the cumulative probability $F[x_{t,j}]$ and further substituting this value in equation 13. This transformation will yield a series with a $N[0,1]$ distribution. The series of $\varsigma_{t,j}$ data will have constant marginal statistics for all parts of the series: the monthly mean, variance, skewness, kurtosis, etc. will all be the same—a prerequisite for applying the ARIMA process to the data. Since the transformation was chosen so that the statistics of the transformed variable are invariant with time, the subscript j on $\varsigma_{t,j}$ may be dropped.

ARIMA Stochastic Process Modeling

Given that the transformed variable is Gaussian with zero mean, variance unity, the ARIMA stochastic difference equation is now relevant to constructing a model for this variable. The system of difference equations for the transformed variable is

$$\phi(B)(1-B)^d\varsigma_t=\theta(B)w_t \tag{14}$$

where w_t is a Gaussian white noise process; B is a backward shift operator defined by $B^r\varsigma_t=\varsigma_{t-r}$; $\phi(B)$ and $\theta(B)$ are polynomials in B defined by

$$\theta(B) = 1 - \theta_1 B - \theta_2 B^2 - \dots \theta_q B^q \tag{15}$$

$$\phi(B) = 1 - \phi_1 B - \phi_2 B^2 - \dots \phi_p B^p \tag{16}$$

If the differenced variable (ie. $(1-B)^d\varsigma_t$) is denotes z_t then the stochastic difference equation is appropriately recast as

$$z_t - \sum_{r=1}^{p}\phi_r z_{t-r} = w_t - \sum_{r=1}^{q}\theta_r w_{t-r} \tag{17}$$

This research will assume that the stochastic process for ς_t may be modeled as having a time invariant autocorrelation structure. A condensed list of the important steps to be followed in applying the $ARIMA[p,d,q]$ process to modeling the historical ς_t series is given by Unny (1977) and Hipel et al (1977). Model construction details are discussed in Box and Jenkins (1970) and Anderson (1976).

System Identification

Identifying the system equations involves studying the stochastic structure of the annual ς_t series to determine the class of models which may be used to represent the data, and which models are worthy of further investigation. The main aim is to obtain an idea of the values of p, d, and q needed in the system equations. The principal tools are the autocorrelation and partial autocorrelation function.

The autocorrelation function ρ_τ in the ς_t data was studied by forming sets of $\{\varsigma_t, \varsigma_{t+\tau}\}$ for $\tau=1$ to 20, and computing the estimated correlation coefficients $\hat{\rho}_\tau$. In this way the linear relationship between values of the transformed variable occurring in month t and values occurring τ previous months to it was studied. These values were computed using twenty years of monthly ς_t data (or differenced ς data). Estimates were obtained using a computer program which systematically extracted the autocorrelation information from zones in the data set where there was no missing data. To identify a model, it is necessary to use estimates $\hat{\rho}_\tau$ to check on whether the autocorrelations are rapidly decaying, or is there any trends. The presence of non-decaying autocorrelation estimates usually indicate the presence of trends, which often suggests the need to difference the data further. If the autocorrelation estimates are decaying, it is also necessary to determine when these estimates are effectively zero beyond a certain lag, τ. For this purpose Bartlett's (1946) approximate expression for the variance of the estimated autocorrelation coefficients of a stationary Normal process can be used to test the statistical significance of autocorrelation estimates.

$$var[\hat{\rho}_{\tau}]=\frac{1}{N}\left[1+2\sum_{v=1}^{q}\hat{\rho}_{v}^{2}\right] \quad \tau > q \tag{18}$$

If the hypothesis is tested that the process is white noise, that is, ρ_{τ} is zero for $q>0$ then the standard error associated with all autocorrelation estimates $\hat{\rho}_{\tau}$ beyond τ equal to zero, will be approximately $(1/N)^{1/2}$; and with N being of the order of 190 (when missing values and loss of information due to differencing are accounted for) the standard error will be approximately 0.073. Figures 1-4 show plots of the autocorrelation at different levels of differencing of Phosphorous and Suspended Sediments in the Thames river. From these plots it is seen that the autocorrelation function for transformed phosphorous data fails to die out, but is significant up to 20 lags. This suggests that the data aught to be differenced. Figure 2 shows that the autocorrelation estimates died out quickly after the first differencing. Additional differencing of this data, as shown in Fig. 3, did not provide for any reduction in the autocorrelation estimates. It was therefore concluded that differencing only once was necessary. On the other hand, when Suspended Sediment data was studied, the autocorrelation estimates of the transformed data all appeared to be insignificant. This suggests that the underlying process is random, and future events does not depend on the time history of the process.

Partial Autocorrelation Function

Before more can be said about the class of models to be entertained it is required to study the partial autocorrelation function. This is done by computing the last parameter in different autoregressive schemes. The class of models to be entertained is determined by studying this quantity (the pacf) in conjunction with the autocorrelation function. The stochastic process may be identified when the last term in an autoregressive scheme is such that estimates for subsequent terms are statistically zero. This activity is an iterative one; it involves assuming different autoregressive schemes to fit to the data, and using the autocorrelation estimates, compute the value of the last parameter in the model. Partial autocorrelation estimates, for values for models of order up to 20, are often required to identify the appropriate model. Obtaining these by solving the Yule-Walker equations can be cumbersome, and costly in computer time; therefore they were computed using a recursive formulae due to Durbin (1960). Durbin's method uses past estimates of the partial autocorrelation function to estimate future values. Thus parameter estimates for an AR[p+1] process are obtained using known estimates of the parameter of an AR[p] process, fitted to the same data. Durbin's formulae are presented as follows:

$$\hat{\phi}_{(p+1)(p+1)}=\frac{r_{p+1}-\sum_{j=1}^{p}\hat{\phi}_{pj}r_{p+1-j}}{1-\sum_{j=1}^{p}\hat{\phi}_{pj}r_{j}} \qquad 19$$

$$\hat{\phi}_{(p+1)j}=\hat{\phi}_{pj}-\hat{\phi}_{(p+1)(p+1)}\hat{\phi}_{p(p-j+1)} \qquad j=1,2,\ldots p \qquad 20$$

Other recursive methods for estimating the partial autocorrelation function have been developed (Pagano, 1973).

Estimates, $\hat{\phi}_{pp}$, of the partial autocorrelation can be obtained by using $p=1,2,3,\ldots$ in equations 19 and 20. These values are then studied to determine when they become statistically indifferent from zero.

Quenouille (1949) states that at large values of τ, the estimated partial autocorrelation is asymptotically normally distributed:

$$\hat{\phi}_{\tau\tau}\sim N\left\{0,\frac{1}{N}\right\}, \quad \tau>p \qquad 21$$

Thus if an autoregressive process is of order p, the estimated partial autocorrelation for an order $p+1$ and higher will be independently distributed with standard error $S.E.[\hat{\phi}_{\tau\tau}]$ of $1/\sqrt{N}$. With N being approximately 190, then Quenouille's formula indicate that twice the standard error of $\phi_{\tau\tau}$ is of the order of 0.15.

Figures 5 and 6 show plots of the partial autocorrelation function for Phosphorous and Suspended Sediments with 95% confidence limits, assuming an hypothesis that they are all zero. The plot for Phosphorous reveal that beyond lag 3 the partial autocorrelation estimates are approximately zero for phosphorous concentration. However, the partial autocorrelation estimates for Suspended Sediments are again insignificant for all lags, thus confirming that all parameters in an autoregressive scheme is statistical zero— hence the process is white noise. Theoretical processes which reveal a truncating partial autocorrelation function are purely autoregressive. Processes with moving average terms have slowly decaying partial autocorrelation function.

The estimated autocorrelation function and the estimated partial autocorrelation function for the differenced data suggest that the process for transformed monthly phosphorous data is autoregressive, and require approximately two (or at most three) parameters for its description. These estimates are, however, themselves correlated and as such should be used only to indicate the type, and neighborhood of the models that should be considered. In general it is necessary to entertain other models than the one indicated to ensure that the most appropriate model, and parsimous model is selected to represent the data. In addition to the ARMA[2,1,0] model, ARMA[3,1,0], and an ARMA[1,1,0] will also be entertained.

Parameter Estimation

Having identified the set of models to be entertained, it is necessary to estimate the parameters in these models, and select the model which fits the data best. There are numerous methods that may be used to estimate the model parameters. The method recommended by Box and Jenkins (1970), and which will be used, is the method of maximum likelihood. Since the variance of ζ_t is constant, and the model is linear, the variance of w_t will also be constant, hence, the conditional log-likelihood function can therefore be studied by studying the conditional sum of squares function. The parameter estimates will therefore be those that minimizes the sum of squares function, or the noise variance. The residuals are the set $\{\hat{w}_t\}$ which minimizes the sum of squares function.

They are obtained using

$$\hat{w}_t = \varsigma_t - \hat{\varsigma}_t \qquad 22$$

where $\hat{\varsigma}_t$ are generated values, obtained using the parameter estimates, and ς_t is the actual data. Different sets $\{\hat{w}_t\}$ can be obtained for various values of (ϕ,θ). The estimation process is made efficient by using a non-linear least squares procedures.

The computation of the sum of squares function is conditional on the starting values for w_t used. For very short series, the transients introduced by the choice of this value, in synthetic data will be significant. However, for fairly long series, the unconditional likelihood function is approximated by the likelihood function, if suitable starting values $w_\bullet$ and $\varsigma_\bullet$ are selected (Box and Jenkins, 1970). For most applications the starting values are set to their unconditional expectation: $E[w_\bullet] = 0$. The parameter estimates will be obtained using zero for the value of w_1.

A modified steepest descent algorithm (IMSL) was used to provide efficient estimates of the parameters that minimized the sum of squares (or noise variance). The estimation was performed using double precision arithmetic. Special care was again necessary, to ensure that the estimation was performed only from zones in the data without missing values. The following tables show summary results from applying ARIMA[1,1,0], ARIMA[2,1,0], and ARIMA[3,1,0] models to ς.

TABLE 4
ARIMA [p,d,q] MODELS FITTED TO TRANSFORMED PHOSPHOROUS DATA

ARIMA[p,d,q] MODEL	PARAM.	PARAM. EST.	PARAM. STD. ERR.	NOISE VAR., σ_w^2
$(1-B)(1-\phi_1 B)\varsigma_t = w_t$	ϕ_1	-0.546	0.060	0.501
$(1-B)(1-\phi_1 B-\phi_2 B^2)\varsigma_t = w_t$	ϕ_1 ϕ_2	-0.679 -0.284	0.054 0.071	0.460
$(1-B)(1-\phi_1 B-\phi_2 B^2-\phi_3 B^3)\varsigma_t = w_t$	ϕ_1 ϕ_2 ϕ_3	-0.725 -0.270 -0.500E-15	0.052 0.073 0.076	0.450

The standard errors of the parameter estimates listed in Table 6 was obtained using the following (Anderson, 1976).

$$ARMA[1,0] : \sigma_\phi^2 = \frac{1-\phi^2}{N} \quad ARMA[2,0] : \sigma_{\phi_1}^2 = \sigma_{\phi_2}^2 = \frac{1-\phi_2^2}{N} \qquad 23$$

A study of the residual variances for the models listed in Table 6 reveal very slight (if any) decrease in unexplained variability for the ARIMA[3,1,0] or ARIMA[2,1,0] models over the ARIMA[2,1,0] model. Anderson (1976) applied the F statistic to give a crude comparison between these noise variances. To test if the ARIMA[3,1,0] model, produces a noise variance that is significantly different from the ARIMA[2,1,0], the computed F will be $(0.46/0.45)^2$, which is 1.045. Testing the hypothesis of equal variance at the 5% significant level, shows $F_{194,183}$, from standard tables, being greater than 1.002. Hence, the variance estimators are not significantly different. A comparison with the ARIMA[1,1,0] model and the ARIMA[2,1,0] model also reveals little or no difference in noise variance. Applying the F test to the ARIMA[1,1,0] and ARIMA[2,1,0] models yields a F statistic of 1.18; and when its significance was tested at the 5% level the difference could have occurred by chance. Hence the most parsimous model for transformed monthly phosphorous data is the ARIMA[1,1,0] model; it is also very significant, since its parameter is approximately eight times its standard error.

Generating Synthetic Water Quality Data

The stochastic models for phosphorous and suspended sediments may be used to generate synthetic water quality data for these monthly events. To do this, it will first be necessary to generate an uncorrelated set of random Gaussian deviates for the w_t process. Many methods for doing this is reported in the literature, examples of which are Marsaglia and Bray (1964), Atkinson and Pierce (1976), and Lewis et al (1969). These white noise random variables are then substituted in the stochastic model to produce synthetic values of the transformed Gaussian variable. Monthly water quality events are then obtained by probability mapping from the Gaussian domain to the domain of the parent distribution. Detail simulation techniques are presented by McLeod and Hipel, 1978.

CONCLUSIONS

In an effort to obtain a greater understanding of the behaviour of toxic contaminants in the Thames river, research into the probability and stochastic features of phosphorous and suspended sediment concentrations have been performed. Mathematical models describing these features have been developed for monthly water quality events. Investigation in the probability behaviour of these events reveal that the governing probability distribution was not fixed for all months, but would change on a monthly basis. These distributions were also observed to be strongly non-Gaussian. The probability density functions were described using a five parameter polynomial expressions. This model successfully preserved the key moments (mean, variance, skewness, and kurtosis) of the historic water quality data.

Stochastic models for the phosphorous and suspended sediment concentrations were developed using the ARIMA process. Since this family of processes require that the underlying distributions for monthly events be Gaussian and time-invariant, novel transformations methods were developed for mapping monthly water quality data from its parent distribution to a N(0,1) distribution, for all months. The model constructed for the transformed monthly phosphorous variable was an ARIMA[1,1,0], with an autoregressive parameter estimate ϕ_1 of -0.546. Transformed suspended sediment data was adequately described using a white noise ARIMA[0,0,0] model.

The modeling methodology developed in this research serves to lay a solid framework for modeling water quality data from various streams. These data are likely to be non-Gaussian and represented by distributions that change monthly. The novel transformation developed in this research for such problems guarantees that the probability distribution of the actual series is incorporated in the model. Hence synthetic water quality events generated using these models are bound to reproduce the complex non-Gaussian time-varying probability distributions, while representing the serial relationship between consecutive monthly events. The foundation laid in this research also allows for stochastic models to be developed for data with substantial missing values, without having to make any assumptions about the character of the missing values. These developed models have the advantage of forecasting probable events for these missing zones, should these be necessary in future study.

REFERENCES

Anderson, O.D. (1976). *Time series analysis and forecasting.* Butterworths, London and Boston.

Atkinson, A.C. and M.C. Pierce (1976). The computer generation of beta, gamma, and normal random variables. Journal Royal Statist. Soc. Ser. A, 4, pp. 139 pp. 431-448.

Bartlet, M.S. (1946). On the theoretical specifications of sampling properties of autocorrelated time series. J. Royal. Statist. Soc. B, 8, pp. 27-41.

Blake, I.F. (1979). *An Introduction to Applied Probability.* Wiley. New Your, Toronto.

Box, G.E.P., and G.M. Jenkins (1970). *Time Series Analysis: Forecasting and Control.* Holden-Day, San Fransisco.

Box, G.E.P. and R.D. Cox (1964). An analysis of transformations. Journal Royal Statist. Soc., B, 26, pp. 211-252.

Durbin, J. (1960). The fitting of time series models. Rev. Int. Ststist. Inst. 28, pp. 233-244.

Frazer, D.A.S. (1976). *Probability and Statistics: Theory and Application.* Wadsworth Publishing Co., Inc. Belmont, California, 94002.

Hipel, K.W. and A.I. McLeod (1979). Modeling seasonal geophysical time series. Technical report no. Xm030579, University of Waterloo.

Hipel, K.W., A.I. McLeod, and W.C. Lennox (1977). Advances in Box-Jenkins modelling, 1, model construction. Water Resource Research 13, pp. 567-575.

Lewis, P.A.W., A.S. Goodman, and J.M. Miller (1969). Pseudo-random number generator for the System 360. IBM System Journal. 8, pp. 136-146.

Marsaglia, G. and T.A. Bray (1964). A convenient method for generating normal variables. SIAM Rev. 6, pp. 260-264.

McLeod, A.I. and K.W. Hipel (1978). Simualtion procedure for Box-Jenkins models. Water Resources Research. 14, pp. 969-975.

Pagano, M. (1973). An algorithm for fitting autoregressive schemes. Journal Royal Statist. Soc. Ser. C. 21, pp. 274-281.

Quenouille, H.M. (1949). Approximate tests for correlation in time series. Journal Royal Stat. Soc., B11, pp. 68.

Snedecor, G.W. and W.G. Cochran (1980) *Statistical Methods.* IOWA State University Press.

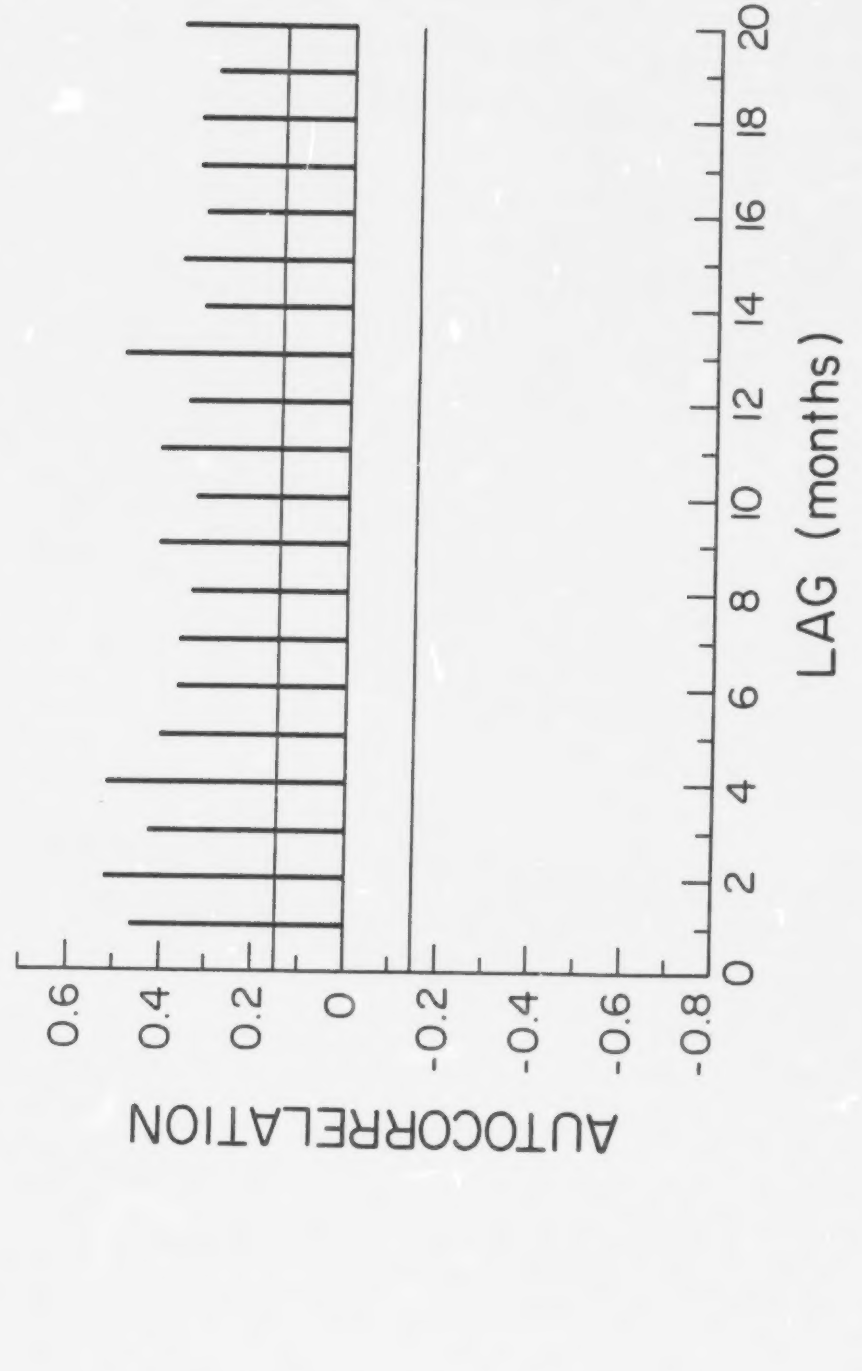
Strecok, A.J. (1968). On the calculation of the inverse error function. Mathematics of Computing, 22, pp. 144-158.

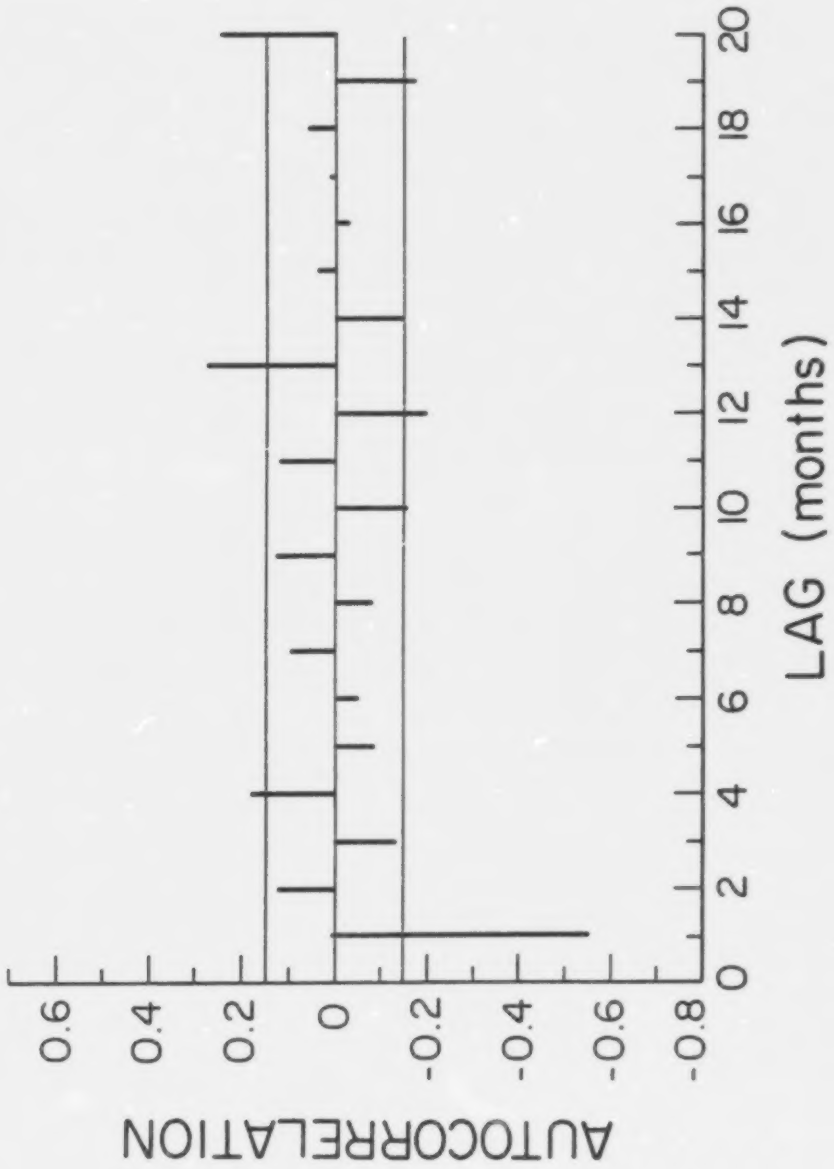
Tao, P.C. and J.W. Delleur (1975). Models of the stochastic and chronologic structure, prediction and simulation of run off sequences-applied to the lower OHIO basin. Purdue University, Water Resources Center. West Lafayette, Indiana. Report #60.

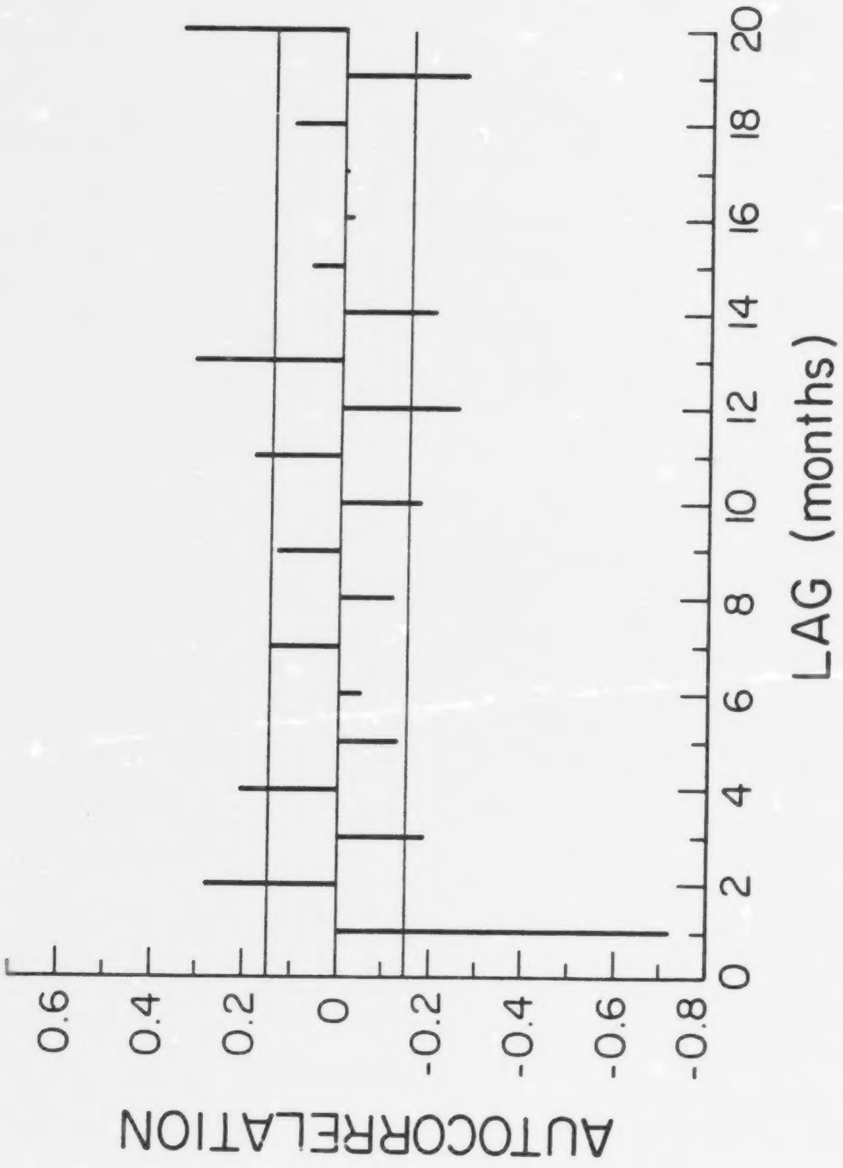
Unny, T.E. (1977). Stochastic precesses in water resources engineering. Proc. 2nd. Int. IAHR Symposium on Stochastic Hydraulics, Lund Inst. of Technology. University of Lund. Lund, Sweden.

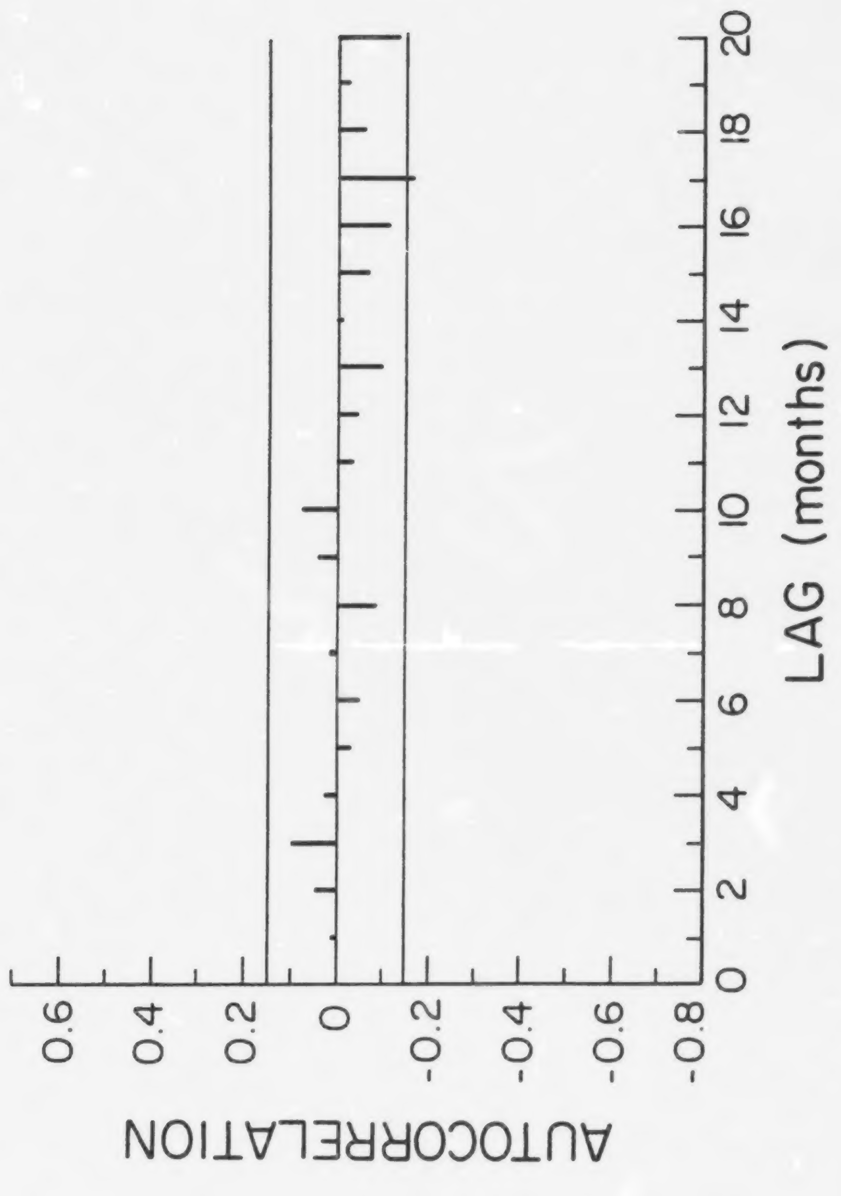
LIST OF FIGURES

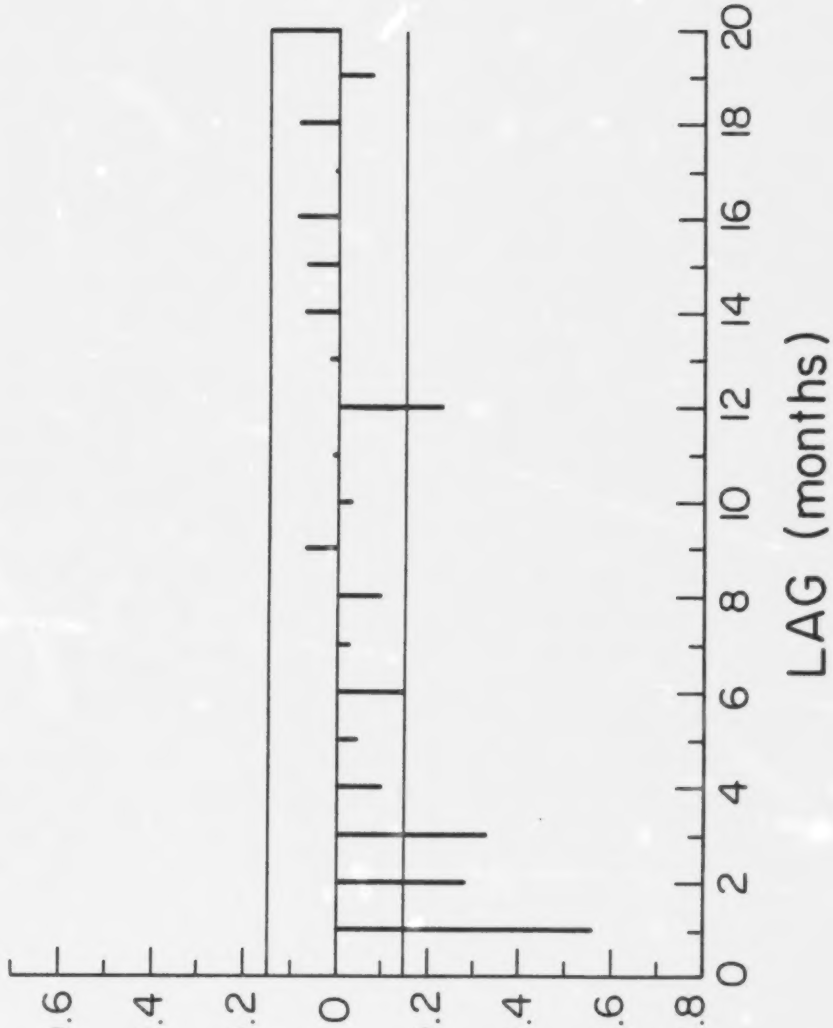
1. Plot of Autocorrelation Function vs Month (Lags) for Transformed Monthly Phosphorous Data
2. Plot of Autocorrelation Function vs Month (Lags) for Once Differenced Transformed Monthly Phosphorous Data
3. Plot of Autocorrelation Function vs Month (Lags) for Twice Differenced Transformed Monthly Phosphorous Data
4. Plot of Autocorrelation Function vs Month (Lags) for Transformed Monthly Sediment Data (Thames River)
5. Plot of Partial Autocorrelation Function vs Month (Lags) for Once Differenced Transformed Monthly Phosphorous Data
6. Plot of Partial Autocorrelation Function vs Month (Lags) for Transformed Monthly Sediment Data

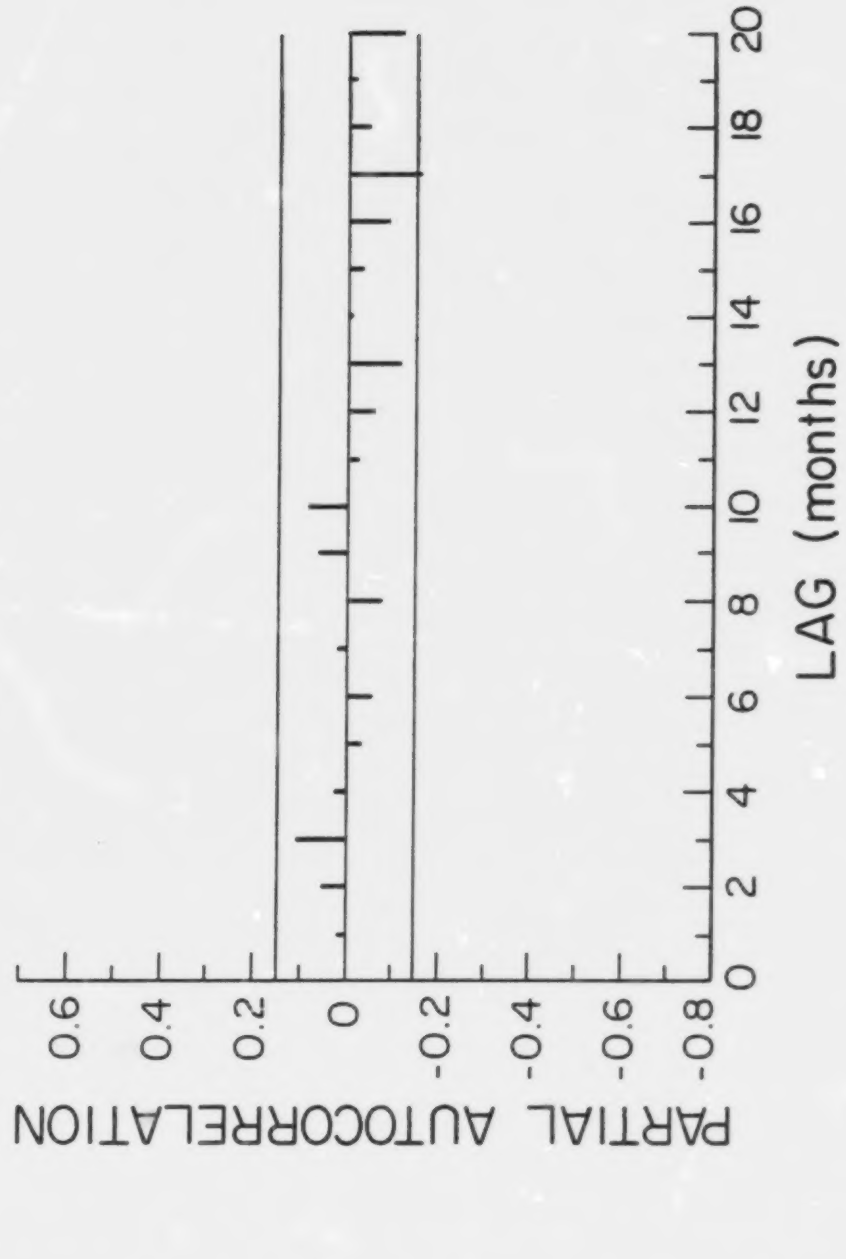

AUTOCORRELATION
0.6
0.4
0.2
0
-0.2
-0.4
-0.6
-0.8
0
2
4
6
8
10
12
14
16
18
20
LAG (months)


AUTOCORRELATION
0.6
0.4
0.2
0
-0.2
-0.4
-0.6
-0.8
LAG (months)
0
2
4
6
8
10
12
14
16
18
20


AUTOCORRELATION
0.6
0.4
0.2
0
-0.2
-0.4
-0.6
-0.8
0
2
4
6
8
10
12
14
16
18
20
LAG (months)


AUTOCORRELATION
0.6
0.4
0.2
0
-0.2
-0.4
-0.6
-0.8
LAG (months)
0
2
4
6
8
10
12
14
16
18
20


PARTIAL AUTOCORRELATION
0.6
0.4
0.2
0
-0.2
-0.4
-0.6
-0.8
0
2
4
6
8
10
12
14
16
18
20
LAG (months)


PARTIAL AUTOCORRELATION
0.6
0.4
0.2
0
-0.2
-0.4
-0.6
-0.8
LAG (months)
0
2
4
6
8
10
12
14
16
18
20

OTTAWA RIVER NUCLEAR SPILL
CONTINGENCY MODEL DEVELOPMENT - PHASE II

by

Rob Jarvis
Gore & Storrie

ABSTRACT

The purpose of the Ottawa River spill model development is to allow contingency planning in the case of a nuclear (probably tritium) spill from the Rolphton nuclear power demonstration (NPD) facility. A model which simulates the two-dimensional - downstream and cross-stream - flow of pollutant already exists in the form of the FORTRAN 77 program TWODIFIN. The purpose of the Phase II Study is to extend this program.

As part of the Phase II Study, a one-dimensional version of the spill model has been developed and implemented in the computer program ONEDIFIN. This is a one-dimensional model - that is, it treats the river as a one-dimensional line and thus assumes complete lateral mixing of pollutant - that can be used to speed up calculations when the pollutant is laterally well-mixed. It is a multiple-source model, so that it can handle simultaneous spills from different locations, and it allows for first-order decay of the radioactive material.

Another major part of the Phase II Study was to interface the one- and two-dimensional programs. In such a hybrid program, the two-dimensional model would be used only for the portion of river that is not laterally well-mixed. Elsewhere, the one-dimensional model would be used, increasing the speed and efficiency of the calculations. This program has been developed and exists in single- and multiple-source versions - ONETWO and OTMULT, respectively.

Along with the main modelling portions, the study also involved the development of computer graphics and other programs to make the model interactive and easy to use. This is proceeding and it is hoped that the graphics will play a major role in helping to analyze and deal with potential spills. Also, model calibration is being performed using field data from the 1981 tritium spill from the Rolphton NPD.

INTRODUCTION

As part of the Ottawa River nuclear spill contingency planning studies, a model which will aid in predicting the arrival times, duration of passage, and concentration distributions of the spilled radionuclide at the water supply intakes and other strategic locations has been developed. This mathematical model consists of a finite-time analytic model that predicts concentration distributions in 2 spatial dimensions (2-D), namely downstream (longitudinal) and cross-stream (lateral). Output from this model can be viewed in two formats i) as a 2-D distribution at a specified time (Figure 2) or ii) as a time varying cross stream distribution at a particular location downstream from the spill.

When the cross-stream distribution reaches a constant value (within a certain margin of deviation) that is, the radionuclide becomes laterally well mixed the computer program switches to a computationaly faster algorithm; a one-dimensional (1-D) finite time model. The one-dimensional part of the computer program varies in time and downstream or longitudinal dimension. Both the 2-D and 1-D are vertically averaged models, that is, the spill material is considered to be vertically well mixed and vertical concentration gradients do not exist.

The remaining objectives of this study are to

1) make the program user-friendly

2) present the model outputs in graphical form

3) perform a calibration and a verification using tracer study data and data from the tritium spill at Rolphton nuclear power demonstration (NDP) facility in 1981.

MODEL FORMULATION

One-Dimensional Spill Model

ONEDIFIN is a Fortran program that produces one-dimensional but time dependant concentration distributions in shallow rivers. This time dependancy allows the modelling of spill events, that is time varying discharges of contaminant into a river. The solution gives concentrations dependent only on the distance downstream from the source of the spill and hence assumes the pollutant to be laterally well-mixed.

The governing equation for the one-dimensional model is:

$$\frac{\partial c}{\partial t} + u \frac{\partial c}{\partial x} = e_x \frac{\partial^2 c}{\partial x^2} - K_d c \qquad (1)$$

where x = longitudinal co-ordinate (m)
t = time (s)
u = velocity downstream (m/s)
e_x = longitudinal dispersion coefficient (m^2/s)
K_d = first order decay rate coefficient (1/s)
c = concentration at location (x) and time (t)

This equation assumes complete vertical and transverse mixing in the river consequently the model, as a whole, is restricted in its application. Generally, the longitudinal distances required to achieve complete vertical and lateral mixing are in the range 50 to 100 times depth and 50 to 100 times width of channel, respectively; for the Ottawa River segment below the Rolphton NDP discharge, the corresponding distances are estimated to be 0.345 and 42.66 km (Gore & Storrie Ltd. 1983). If there is any uncertainty, a two-dimensional model can be used to determine when the river becomes laterally mixed (vertical mixing will already have occurred by this point downstream).

The solution to the equation under a release of pollutant of constant discharge and concentration is:

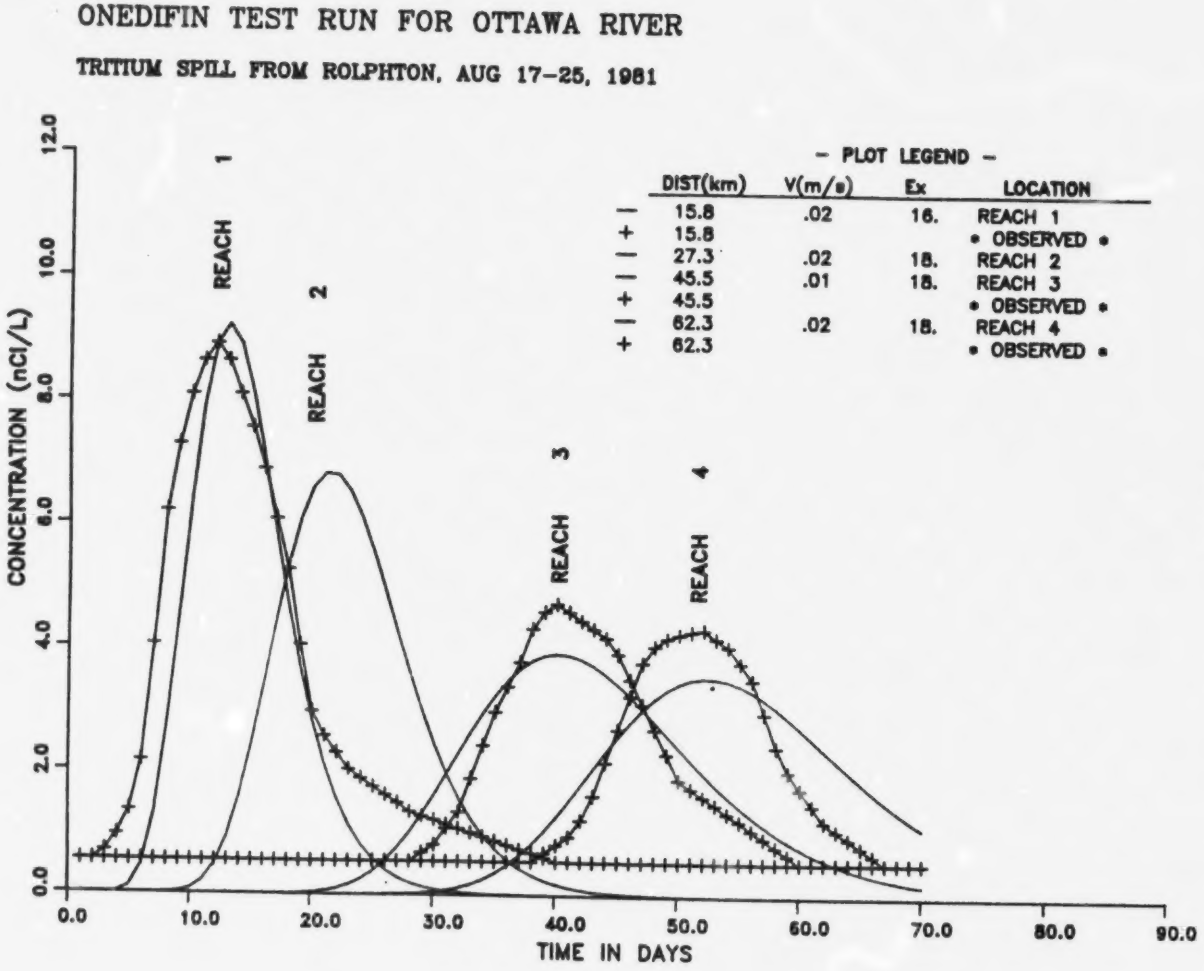


FIGURE 1
Output from model
ONEDIFIN

$$c = \frac{w}{2Au} \quad e^{(ux/e_x)} \left\{ \operatorname{erf}\left(\sqrt{\frac{a}{t-t_i}} + \sqrt{b(t-t_i)}\right) - \operatorname{erf}\left(\sqrt{\frac{a}{t-t_j}} + \sqrt{b(t-t_j)}\right) + \operatorname{erf}\left(\sqrt{\frac{a}{t-t_j}} - \sqrt{b(t-t_j)}\right) - \operatorname{erf}\left(\sqrt{\frac{a}{t-t_i}} - \sqrt{b(t-t_i)}\right) \right\} \quad (2)$$

where $a = x^2/4e_x$ (2a)

$b = (u^2/4e_x) + K_d$ (2b)

$w = c_o q_o$ (2c)

and x = distance from source (m)

t = time (s)

c_o = concentration of source release

q_o = discharge of source (m^3/s)

A = cross-sectional area of flow (m^2)

u = velocity of flow (m/s)

e_x = longitudinal dispersion coefficient

t_i = time of the start of the release (s)

t_j = time of the end of the release (s)

To obtain a complete solution, it is necessary to break the release of pollutant up into short intervals such that the discharge and concentration is relatively constant over each. Using the linearity of Equation 1, these partial solutions can be summed for each (x,t) (See Figure 1).

In ONEDIFIN, each reach is treated in isolation, with a "source" at the beginning and the concentration calculations being made at the end. The mass discharge value, w, from Equation 2 is determined for each reach by combining the calculated results from the previous reach and the inputs from any new sources at the beginning of the reach. In other words, the flow of pollutant from the previous reach is treated as a source and added to the flow from any other sources. This technique is much faster than superposition when multiple sources are being considered.

Two-Dimensional Spill Model

TWODIFIN is an acronym for TWO-DImensional FINite-time model. The "two-dimensional" part refers to the two spatial dimensions that it considers - the longitudinal or downstream dimension and the lateral or cross-stream dimension. As in the case of ONEDIFIN, the finite-time part refers to the fact that the model is driven by a spill event (see Figure 2).

This model is made tractable through the use of a transformation in the lateral dimension known as the stream tube method. The fundamental concept of the stream tube model developed by Yotsukura and Cobb (1972) is that it uses the cumulative partial discharge, q, at a given cross-section instead of the lateral discharge, y, as independant variable. In this approach, the cross-section is divided into a number of vertical strips termed "stream tubes" such that the discharge within each stream tube is equal. Thus, the cross-sectional concentration distributions c(x,q), predicted by the stream tube model will be functions of q. These distributions can be transformed into c(x,y) as a function of distance from the bank, y, by knowing the relation between q and y at each transect.

The derivations of the basic equations of the stream tube model have been presented by Yotsuhura and Cobb (Ibid); they are subject to the following assumptions.

1. The density of the effluent (or solute) is the same as that of the receiving water. This assumption is reasonably satisfactory for most of the municipal effluent discharges to rivers.

2. The concentration distributions in the far field are not effected by the near field mixing processes (eg. dilution due to initial momentum of jet). Usually, the jet-induced diffusion approaches the ambient diffusion for a short distance below a source in a shallow river.

3. The depth distribution of effluent in the river channel is uniform. Generally the longitudinal distance required to attain depth uniformity is short in shallow rivers, being of the order of 50 to 100 times the channel depth; thus, this assumption is justified.

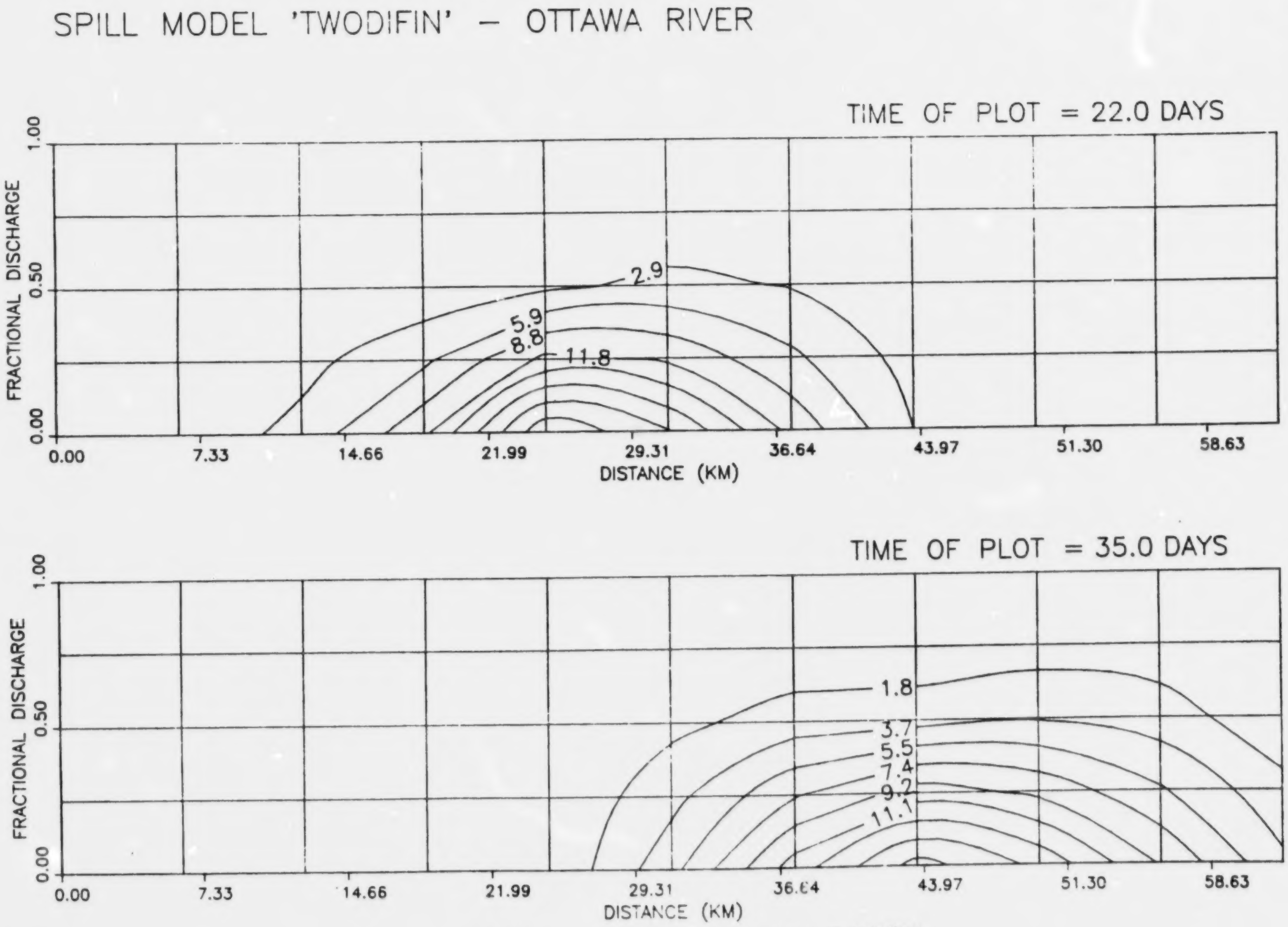


FIGURE 2 Output from model TWODIFIN

The Convective - Dispersion Equation

The 2-D convective-dispersion equation for a non-conservative material in the far field region of the mixing zone can be written in the form:

$$\frac{\partial c}{\partial t} + u\,\frac{\partial c}{\partial x} = e_x\,\frac{\partial^2 c}{\partial x^2} + uD_y\,\frac{\partial^2 c}{\partial q^2} - K_d c \qquad (1)$$

where x = longitudinal co-ordinate (m)

q = lateral co-ordinate (m^3/s)

t = time (s)

u = velocity of flow in the x direction (m/s)

e_x = longitudinal dispersion coefficient (m^2/s)

D_y = lateral diffusion factor (m^5/s^2)

K_d = first order decay rate coefficient (1/s)

c = concentration at point (x,q) at time (t)

The solution to the equation under a release of pollutant of constant discharge and concentration is:

$$C = \frac{u.}{4}\;\frac{\exp\left(\frac{ux}{2e_x}\right)}{\sqrt{\pi e_x e_q}}.W.\;\frac{\exp\left(-2\sqrt{ab}\right)}{(ab)^{1/4}}\left\{\operatorname{erf}\left(\sqrt{\frac{a}{t-t_j}} - \sqrt{b(t-t_j)}\right)\right.$$

$$\left. - \operatorname{erf}\left(\sqrt{\frac{a}{t-t_i}} - \sqrt{b(t-t_i)}\right)\right\} \qquad (2)$$

where $a = (x^2/4e_x) + ((q_s - q)^2/4e_q$ (2a)

$b = (u^2/4e_x) + K_d$ (2b)

and u = velocity of flow (m/s)

x = distance downstream from source (m)

t = time (s)

t_i = time of beginning of release (s)

t_j = time of end of release (s)

w = rate of release of mass (1/s)

e_x = longitudinal dispersional coefficient (m^2/s)

e_q = transverse diffusion coefficient (m^6/s^3)

The transverse diffusion coefficient is calculated in the TWODIFIN model using the relation:

$$e_q = \beta Q^2 u/b \qquad (3)$$

where Q is the total discharge for a reach and β is a dimensionless factor to be estimated from field river data. This can be done by making several runs of the model with different β-values and choosing the value that produces the most realistic lateral mixing distance. Typically, its value ranges from .0005 to .01 (see Appendix A).

As in the case of the 1-D model, a complete solution for a spill with time-varying discharge and concentration can be developed by breaking the spill into small elements and summing the result of Equation 2 for each element.

The program TWODIFIN considers sidewall reflection effects using the method of images.

In TWODIFIN, the river is divided longitudinally into reaches, and laterally into stream tubes. Each reach should be a river section of fairly constant hydrodynamic characteristics; TWODIFIN uses constant dispersion coefficients within each reach. The position of the stream tube boundaries are determined only at transects where the velocity, depth and width measurements have been surveyed.

TWODIFIN considers only a single source, at the beginning of the first reach. The reaches are not treated independently, as they are in ONEDIFIN, where the pollutant flow from the previous reach serves as the "source" for the current one. Instead, the concentration is calculated for each reach from the flow of pollutant from the source all the way to the end of the reach. To take into account the variation of hydrodynamic parameters from reach-to-reach, moving averages are maintained that approximate the effective values of river width, depth, and velocity of flow.

Hybrid Spill Model

Aside from ONEDIFIN and TWODIFIN, there is also a hybrid spill model, ONETWO. In this program, calculations are made according to the 2-D model until the river becomes well-mixed, at which point the 1-D model is used. This is useful for studying long rivers, in which lateral mixing occurs a short distance downstream in relation to the total length studied, because the 1-D model is much faster than the 2-D version.

Like the two other models mentioned above, ONETWO is a finite-time model. It is also a multiple source model which, unlike ONEDIFIN, accepts sources placed anywhere along the river. The resulting concentration predictions are obtained by superposition method (explained below). This method has disadvantages: principally, it is slower than the method used in ONEDIFIN, by a factor equal to the number of sources used. However, it separates source placement from reach definition, which are unrelated procedures, and it does not suffer the mass-loss problems encountered by ONEDIFIN when going from reach to reach.

ONETWO calculates the pollutant distribution using the method of superposition. That is, it considers each source separately and determines the concentration distribution which that source would cause if it were the only one on the river. It then sums these distributions (by algebraically summing the concentration predictions together for each location and time) to obtain the complete solution. This can be done whether a 1-D or 2-D model is being used. This approach is justified because the equations are linear in concentration.

The criterion that ONETWO uses to determine the reach at which the river becomes well-mixed involves a simple ratio test. Specifically, when the ratio between the minimum and maximum concentrations across the river for that reach is greater than some tolerance value, the river is said to be well mixed. This tolerance will usually have a value of 0.8 or 0.9.

APPENDIX A

EVALUATION OF DISPERSION COEFFICIENTS

Two dispersion coefficients are used in the spill model. The longitudinal coefficient determines the downstream spread of the pollutant and the lateral dispersion coefficient determines the cross-stream spread. The lateral coefficient is used only in the two-dimensional model.

The longitudinal dispersion coefficient e_x has untis m^2/s. There are several different methods for calculating e_x but in the context of this model it becomes primarily a matter of empirical calibration. The user adjusts e_x in the model reach by reach unit predictions match observed data. The model is set-up so that after an e_{x1} has been determined at a measured total river flow Q_1, e_{x2} can be determined knowing a different total flow Q_2. This scale up method was derived from the Leopold-Maddock relationships. According to

$$e_x = 22.6\, n\, \overline{u}\, \overline{d}^{5/6} \qquad \text{(A.1)}$$

where n = Manning's "n" $(m^{1/6})$
$\overline{u}$ = average water velocity
$\overline{d}$ = average depth

The Leopold-Maddock relationships are;

$$\overline{u} = bQ^{vex} \quad \text{or} \quad \overline{u}_2 = \overline{U}_1(Q_2/Q_1)^{vex} \qquad \text{(A.2)}$$

$$\overline{d} = cQ^{hex} \quad \text{or} \quad \overline{d}_2 = \overline{d}_1(Q_2/Q_1)^{hex} \qquad \text{(A.3)}$$

$$W = eQ^{wex} \quad \text{or} \quad W_2 = W_1(Q_2/Q_1)^{wex} \qquad \text{(A.4)}$$

where $\overline{udw} = Q$ and w is top width.

The parameters VEX, HEX and WEX are determined empirically and must sum to unity. From equations A.1, A.2 and A.3 we get

$$ex_2 = ex_1\left(\frac{Q_2}{Q_1}\right)^{vex + 5/6\, hex}$$

Typical values for a shallow river are

HEX = .50
VEX = .45
WEX = .05

and therefore

$$ex_2 = ex_1\ (Q_2/Q_1)^{.8667}$$

The lateral dispersion coefficient has units m^6/s^3. TWODIFIN calculates it using the equation

$$e_q = \beta Q^2 u/b \tag{2}$$

where e_q = lateral dispersion coefficient (m^6/s^3)
β = dimensionless dispersion factor
Q = discharge of the river (m^3/s)
u = velocity of flow (m/s)
b = river width (m)

Like the regional dispersion factor in Equation 1, the factor, β, is essentially a calibration factor, which in this case, adjusts the lateral dispersion coefficient to a more realistic value. It can be determined by any of a number of relationships, but these are not always reliable. If some actual river data is available, it will probably be more accurate to use trial-and-error.

Trial-and-error estimation of e_x can be done in a couple of ways. If actual dispersion coefficients are known for the river in question, it is a simple matter to solve for the appropriate β-values (β is not a constant - it can vary with respect to downstream distance). If concentration profiles are known from direct measurement, the TWODIFIN model can be run with different β's, and those that give the best prediction can be selected.

REFERENCES

Bansal, M.K., 1971. Dispersion in Natural Streams. Journal of Hydraulics Division, ASCE, 97 (HY11): 1867-1886.

Beltaos, S., 1979. Transverse Mixing in natural Streams. Canadian Journal of Civil Engineering. 6 (4): 575-591.

Fisher, H.B., 1967. The Mechanics of Dispersion in Natural Streams. Journal of Hydraulics Division, ASCE, 93 (HY6): 187-216.

Glover, R.E., 1964. Dispersion of Dissolved or Suspended materials in Flowing Streams. U.S. Geol. Survey Prof. Paper 433-B, 32 p.

Gore & Storrie, Ltd., 1983. Dispersion Estimates for the Ottawa River Nuclear Spill Contingency Model. Technical Report prepared for the Ontario Ministry of the Environment, Toronto, Ontario. 34 p.

Gowda, T.P.H., 1980. Stream Tube Model for Water Quality Prediction in Mixing Zones of Shallow Rivers. Water Resources Paper 14, Water Resources Branch, Ontario Ministry of the Environment, Toronto.

Gowda, T.P.H., 1981. Water Quality Prediction in Shore-Attached Mixing Zones in Rivers. An Assessment Procedure prepared for Working Group II of the Water Management Steering Committee, Ontario Ministry of the Environment, Toronto, Canada, 59 p.

Gowda, T.P.H., 1984a. Critical Point Method for Mixing Zones in Rivers. Journal of Environmental Engineering, ASCE, 110 (1): 244-262.

Gowda, T.P.H., 1984b. Water Quality Prediction in Mixing Zones of Rivers. Journal of Environmental Engineering, ASCE, 110 (4): 751-769.

Hamdy, Y., 1981. Dispersion of Effluent Plumes from Diffusers on Near-Shore Regions of the Great Lakes, Vol. 1 - Initial Mixing Processes. Ontario Ministry of the Environment, Toronto.

Heathcote, I.W., 1982. Spills Dispersion. Grand River Basin Water Management Study, Technical Report No. 31, Water Resources Branch, Ontario Ministry of the Environment, Toronto (Draft).

Henry, J.F., and Foree, E.G., 1979. Dispersion Modelling in Time and Two Dimensions. Journal of the Environmental Engineering Division, ASCE, 105 (EE6): 1131-1147.

McQuivey, R.S. and Keefer, T.N., 1976. Convective Model of Longitudinal Dispersion. Journal of Hydraulics Division, ASCE, 102 (HY10): 1409-1424.

Medina, M.A., Jr. and Buzun, J., 1981. Continuous Simulation of Receiving Water Quality Transients. Water Resources Bulletin, 17 (4): 549-557.

Sagar, B., 1982. Dispersion in Three Dimensions: Approximate Analytic Solutions. Journal of Hydraulics Division, ASCE, 108 (HY1): 47-62.

Wnek, W.J. and Fochtman, E.G., 1972. Mathematical Model for Fate of Pollutants in Near-Shore Waters. Environmental Science and Technology, 6 (4): 331-337.

Yotsukura, N. and Cobb, E., 1972. Transverse Diffusion of Solutes in Natural Streams. U.S. Geological Survey Professional Paper 582-C, U.S. Government Printing Office, Washington, D.C., 19 p.

Yotsukura, N. and Sayre, W., 1976. Transverse Mixing in Natural Channels. Water Resources Research, 12 (4): 695-704.

Volume

3

ISSN 0-829-9706

ABSTRACTS

TECHNOLOGY TRANSFER CONFERENCE

December 8 & 9, 1986

The Sheraton Centre

External Research Projects

Organized by
Research Advisory Committee

Sponsored by

Corporate Resources Division
Ministry of the Environment
Ontario
CANADA

INTRODUCTION

The Ontario Ministry of the Environment holds its annual Technology Transfer Conference to report and publicize the progress made on Ministry-funded environmental and health-related research projects. These studies are carried out in Ontario universities and by private research organizations.

This booklet presents the abstracts of the papers presented at Technology Transfer Conference, held in December 1986. The abstracts are divided into five sections, corresponding to the conference sessions, dealing with air quality research, water quality research, liquid and solid waste research, analytical methods and instrument development as well as environmental economics.

For further information on any of the projects, the reader is kindly referred to the Conference Proceedings, (ISSN 0-825-4591), or to the principal investigators.

Goal Statement

"To achieve and maintain a quality of the environment - including air, water and land - that will protect human health and the ecosystem and will contribute to the well-being of the people of Ontario."

ACKNOWLEDGEMENTS

The Conference Organization Committee would like to thank the speakers and organizers for their valuable contributions.

DISCLAIMER

The views and ideas expressed in these papers are those of the authors and do not necessarily reflect the views and policies of the Ministry of the Environment, nor does mention of trade names or commercial products constitute endorsement or recommendation for use.

Paper No. **Page No.**

INTRODUCTION ii

KEYNOTE PAPERS

I CRUCIAL ISSUES IN ENVIRONMENTAL TOXICOLOGY 2
G. Plaa: Vice-Dean of Medical Research and Graduate Studies, University of Montréal, Québec, Canada.

II SOME INTERNATIONAL DEVELOPMENT IN ENVIRONMENTAL ASPECTS OF INDUSTRIAL AND TECHNOLOGICAL ACTIVITIES 3
F. Roots: Science Advisor, Environment Canada, Ottawa, Ontario, Canada.

III THE US-EPA PROGRAM TO EVALUATE THE EFFECTS OF TOXIC CHEMICALS 5
J. Falko: Director, Office of Environmental Processes and Effects Research, US-EPA, Washington, D.C., U.S.A.

SESSION A: AIR QUALITY RESEARCH:

FEATURE PAPERS

A AN OVERVIEW OF ALBERTA ENVIRONMENT'S DEPOSITION RESEARCH PROGRAM 7
H.P. Sims: Director, Alberta Environment's Research Management Division, Alberta, Canada.

B MULTIMEDIA ANALYSIS AND ASSESSMENT OF ENVIRONMENTAL TOXIC AND CARCINOGENIC SUBSTANCES ... 8
R. Harkov: Office of Science and Research, New Jersey Dept. of Environmental Protection, New Jersey, U.S.A.

SESSION PAPERS

1 THE RAPID SCREENING OF MUNICIPAL REFUSE INCINERATOR FLYASH AND STACK GAS FOR PCDD/PCDF USING A TRANSPORTABLE TANDEM MASS SPECTROMETER (GC/MS/MS) SYSTEM 9
B. Shushan[1], A. Ngo[1], V. Ozvacic[2], G. Wong[2], G. DeBrou[2], B. Bobbie[2], R. Clement[2], S. Thorndyke[3] and B. Chittum[4]. 1-SCIEX, 2-Environment Ontario, 3-ORF, 4-Willington Consultants.

Paper No.		Page No.
2	**RETROSPECTIVE CORRELATION SPECTROSCOPY AND ITS APPLICATION TO ATMOSPHERIC MONITORING** ..... R.W. Nicholls, M. Amani, M. Mandelman and W. Morrow, York University, Toronto, Ontario.	10
3	**MEASUREMENT OF ATMOSPHERIC CONSTITUENTS BY TUNABLE DIODE LASER ABSORPTION SPECTROMETRY** .... H.I. Schiff, York University, Toronto, Ontario.	11
4	**UPTAKE, DISTRIBUTION AND CLEARANCE OF SOLUBLE AEROSOLS IN THE HUMAN RESPIRATORY SYSTEM** .... W.J. Megaw[1] and J.F. Hicks[2]. 1-York University, Toronto, and 2-Environment Ontario.	12
5	**EXPERIMENTALLY DETERMINED MUTATION RATES IN LUNG AS AN AIR QUALITY STANDARD** .... J. Heddle, A. Bouch, C. Couch, H. Kaul, J. Gingerich and K. Jain, York University, Toronto, Ontario.	13
6	**THE HAMILTON STUDY: EFFECTS OF FINE PARTICLES ON THE RESPIRATORY HEALTH OF SCHOOL CHILDREN** .... L.D. Pengelly, A. Kerigan, C. Goldsmith, W. Furlong and S. Toplack, McMaster University, Hamilton, Ontario.	14
7	**BIOLOGICAL MONITORING OF ENVIRONMENTAL GENOTOXICITY** .... M. Petras, J. Norsworthy, M. Vrzoc, and K. Hill, University of Windsor, Windsor, Ontario.	15
8	**FIELD AND LABORATORY VALIDATION OF A HIGH-VOL DENUDER FOR MINIMIZING PAH OXIDANT REACTIONS** .... C.S. Davies[1], S. Guerin[1], J. Marr[2] and M. Quilliam[2]. 1-Concord Scientific Corp., 2-McMaster University, Ontario.	16
9	**A PARTICLE-SIZE SPECIFIC ELEMENTAL MASS BALANCE FOR APPORTIONMENT OF AMBIENT AEROSOL SAMPLED WITH MULTISTAGE FRACTIONATORS** .... R.E. Jervis and T. Pringle, University of Toronto, Toronto, Ontario.	17
45	**MUTAGENICITY OF COMPLEX MIXTURES OF PAHS' IN AMBIENT AIR PARTICULATE MATTER** .... A.S. Raj and M. Katz, York University, Toronto, Ontario.	18

Paper No. Page No.

46 DOSE - RESPONSE STUDIES OF GASEOUS POLLUTANTS OF FOOD CROPS 20
D.P. Ormrod and J. Petite, University of Guelph, Guelph, Ontario.

47 PRODUCTION OF OZONE INSENSITIVE WHITE BEAN VARIETIES 21
T.E. Michaels, University of Guelph, Guelph, Ontario.

48 NICKEL CARBONYL AMBIENT MONITOR 22
D.R. Hastie and H.I. Schiff, York University, Toronto, Ontario.

49 ELEMENTAL COMPOSITION OF AIR PARTICULATES INSIDE AND OUTSIDE A BUILDING 23
P. Harvey, J.D. McArthur and G. Palmer, Queen's University, Toronto, Ontario.

50 STUDY OF THE THERMAL REACTIONS OF PCDD ON FLYASH PARTICLES UNDER INCINERATOR CONDITIONS 24
L.C. Dickson and F.W. Karasek, University of Waterloo, Waterloo, Ontario.

51 CONTINUOUS EMISSION MONITORING FOR TOTAL HYDROCARBON AT SEWAGE SLUDGE INCINERATORS 25
J. Kosch, AMKO Systems Inc., Thornhill, Ontario.

52 STUDY OF THE SPATIAL DISTRIBUTION OF THE IMPACT OF SUDBURY SMELTING EMISSIONS 26
E.A. McBean, J. Byrne, J. Donald and G. Farquhar, University of Waterloo, Waterloo, Ontario.

53 CHARACTERIZATION OF BUILDING WAKE EFFECTS AT DARLINGTON NUCLEAR GENERATING STATION USING SULPHUR HEXAFLUORIDE AS A TRACER 27
G. Ogram[1], H. Sahota[2] and P.K. Misra[2].
1-Ontario Hydro, 2-Environment Ontario.

SESSION B: WATER QUALITY RESEARCH

FEATURE PAPERS

A PREDICTIVE MODELS IN HAZARD ASSESSMENT OF GREAT LAKES CONTAMINANTS OF FISH 29
Dora R. May Passino: U.S. Fish and Wildlife Service, National Fisheries Centre - Great Lakes, Ann Arbor, Michigan, U.S.A.

Paper No. Page No.

B CONTROL OF TOXIC TRACE CONTAMINANTS IN MUNICIPAL WASTE WATER TREATMENT PLANTS 30
Henryk Melcer: Biological Processes Section, Wastewater Technology Centre, Canada Centre for Inland Waters, Environment Canada, Burlington, Ontario, Canada.

SESSION PAPERS

10 TRACE ORGANIC CONTAMINANT REMOVAL FROM DRINKING WATER 31
J. Hilton, MacLaren Plansearch Inc., Toronto, Ontario.

11 THE ROLE OF ORGANIC CARBON IN CONTROLLING THE OCCURRENCE OF DENITRIFICATION IN GROUNDWATER 32
R.C. Starr and R.W. Gillham, University of Waterloo, Waterloo, Ontario.

12 REPRODUCTIVE OUTCOMES IN SOUTHWESTERN ONTARIO, 1980 TO 1985 33
J. McD. Robertson, H. Chan and I. Fyfe, University of Western Ontario, London, Ontario.

13 ORGANIC CONTAMINANT STRUCTURE - PROPERTY - TOXICITY RELATIONSHIPS FOR AQUATIC ORGANISMS 34
S. Abernethy and D. Mackay, University of Toronto, Toronto, Ontario.

14 EFFECT OF LEAD, CADMIUM AND MERCURY ON THE TISSUE OF YOUNG FISH AND RATS: DEVELOPMENT OF BIOINDICATOR 35
D.M. Nicholls, R. Angelow, K. Tiechert-Kuliszewska and G. Girgis, York Univesity, Toronto, Ontario.

15 IN-SITU ASSESSMENT OF MIXED COPPER AND ZINC IMPACTS ON WHITE SUCKER (Castastomus Commersoni) POPULATIONS IN SEVERAL NORTHERN ONTARIO LAKES: AN EVALUATION OF THE ENVIRONMENTAL HEALTH APPROACH TO VALIDATING WATER QUALITY CRITERIA 36
K.R. Munkittrick and D.G. Dixon, University of Waterloo, Waterloo, Ontario.

16 THE FATE OF TOXIC ORGANIC CHEMICALS IN SEWAGE TREATMENT PLANTS 37
B. Clark, S. Salenicks, J. Glynn Henry and D. MacKay, University of Toronto, Toronto, Ontario.

17 TOXICITY OF PENTACHLOROPHENOL TO ZOOPLANKTON 38
N.K. Kaushik and G. Stephenson, University of Guelph, Guelph, Ontario.

Paper No.		Page No.
18	DEVELOPMENT OF A STANDARD CLAM BIOMONITORING METHODOLOGY FOR THE DETECTION OF TRACE CONTAMINANTS WITHIN WATERS OF THE ONTARIO GREAT LAKES REGION .... A. Melkic, E. Greece and D. Lewis, Integrated Explorations Ltd., Guelph, Ontario.	39
54	EVALUATION OF DATA ON THE EFFECTS OF HYDRAULIC CHARACTERISTICS AND EFFLUENT CHLORINATION ON THE INCIDENCE OF MICRO-ORGANISMS OF PUBLIC HEALTH SIGNIFICANCE IN RECEIVING WATERS .... M. Palmer, Gore & Storrie Ltd., Toronto, Ontario.	40
55	LISTOWEL ARTIFICIAL MARSH TREATMENT PROJECT .... J. Herskowitz, S. Black and W. Lewandowski, Ministry of the Environment, Toronto, Ontario.	41
56	A LOW PRESSURE HYDROCYCLONE FOR USE IN SEWAGE TREATMENT .... J.D. Boadway, Queen's University, Kingston, Ontario.	42
57	THE EFFECTS OF RURAL AND SUBURBAN DEVELOPMENT ON SURFACE WATER QUALITY IN FIVE SELECTED SUBWATERSHEDS ON THE UPPER HUMBER RIVER .... B. Hindley, R. Hubbard and S. Maude, Metro Toronto Conservation Authority, Toronto, Ontario.	43
58	HUMBER RIVER/BLACK CREEK: DETAILED BACTERIOLOGICAL WATER QUALITY STUDY EXAMINING THEIR IMPACT OF SEDIMENT AND SURVIVAL TIMES .... P.L. Seyfried and E. Harris, University of Toronto, Toronto, Ontario.	44
59	FEASIBILITY OF PLANT HARVESTING IN WATER QUALITY AMELIORATION AND PHOSPHORUS MANAGEMENT IN SHALLOW IMPOUNDMENT .... P. McKee, K. Clarke-Whistler and G. Gaspardy, Beak Consultants Ltd., Toronto, Ontario.	35
60	TWO BIOASSAYS FOR THE RAPID DETERMINATION OF THE EFFECTS OF DREDGED SEDIMENT DISPOSAL IN PRIMARY PRODUCTION AND PHOSPHORUS KINETICS IN OPEN WATERS .... C. Ewing and C. Nalewajko, University of Toronto, Scarborough, Ontario.	46
61	STOCHASTIC ESTIMATION OF AMBIENT WATER QUALITY IN THE THAMES RIVER .... V.A. Graham, T.E. Unny and L. Logan, University of Waterloo, Waterloo, Ontario.	47
62	OTTAWA RIVER NUCLEAR SPILL CONTINGENCY MODEL DEVELOPMENT: PHASE II .... T. Gowda, M. Palmer, C. Arnoldi and R. Jarvis, Gore & Storrie Ltd., Toronto, Ontario.	48

Paper No. **Page No.**

SESSION C: LIQUID & SOLID WASTE RESEARCH

FEATURE PAPERS

A HAZARDOUS WASTE DESTRUCTION: AN OVERVIEW OF APPROACHES AND SHORTCOMINGS 50
E. Timothy Oppelt: Thermal-Destruction Branch, Alternative Technologies Division, U.S.-EPA, Cincinnati, Ohio, U.S.A.

B AN OUTLINE OF U.S.-EPA RESEARCH ON LAND DISPOSAL OF HAZARDOUS WASTE 51
Norbert Schomaker: Hazardous Waste Engineering Research Lab., US-EPA, Cincinnati, Ohio, U.S.A.

SESSION PAPERS

19 ASSESSMENT OF A PROTOTYPE SYSTEM FOR PYROLYSIS OF REFUSE DERIVED FUEL 52
S.J. Thorndyke, Ontario Research Foundation, Mississauga, Ontario.

20 MUNICIPAL SOLID WASTE FEASIBILITY OF GASIFICATION WITH PLASMA ARC 53
G.W. Carter, Resorption Canada Ltd., Ottawa, Ontario.

21 SEWAGE SLUDGE COMPOST AS TURF FERTILIZER 54
J.L. Eggens, Ontario Agricultural College, University of Guelph, Guelph, Ontario.

22 WASTE MANAGEMENT PLANNING FOR PHARMACEUTICAL INDUSTRY - PHASE I: INVENTORY AND DATA COLLECTION 55
R. Makhija and R. Stairs, Tent University, Peterborough, Ontario.

23 DEVELOPMENT OF GUIDELINES FOR THE UTILIZATION OF INDUSTRIAL WASTE IN BACKFILL AND CONSTRUCTION APPLICATIONS 56
G. Zukovs, Canviro Consultants Ltd., Toronto, Ontario.

24 NUMERICAL AND LABORATORY MODELLING OF TWO-PHASE FLOW IN POROUS MEDIA: 1 - TWO-PHASE GASEOUS FLOW, 2 - TWO-PHASE LIQUID FLOW 57
G. Farquhar, E. McBean, J. Byrne, W. Abbott and R. Kell, University of Waterloo, Waterloo, Ontario.

Paper No.		Page No.
25	**DEVELOPMENT OF POLYSULFIDE TECHNOLOGY FOR TREATMENT OF CONCENTRATED SPENT CYANIDE LIQUORS** ... J.J. Gaczarczyk, University of Toronto, Toronto,	58
26	**TREATMENT OF LANDFILL LEACHATE BY SPRAY IRRIGATION** .... R. McBridge, A.M. Gordon, P. Groenvelt, T. Bates and K. King, University of Guelph, Guelph, Ontario.	59
27	**CO-DISPOSAL OF INDUSTRIAL AND MUNICIPAL WASTES: PART II** .... D. Kirk and M. Lau, University of Toronto, Toronto, Ontario.	60
63	**HAZARDOUS ORGANIC CHEMICALS IN GROUNDWATER AT ONTARIO LANDFILLS.** .... J.F. Baker and J. Cherry, University of Waterloo, Waterloo, Ontario.	61
64	**DISPERSION OF THE STOUFFVILLE CONTAMINANT PLUME** .... I. Proulx, R.N. Farvolden and E. Frind, University of Waterloo, Waterloo, Ontario.	62
65	**DEVELOPMENT OF DESIGN CRITERIA FOR OPTIMAL RECOVERY OF LEACHATE UNDER SANITARY LANDFILLS** .... L. Arnaud, E. Frind, R. Farvolden and R. Gillham, University of Waterloo, Waterloo, Ontario.	63
66	**AN INVESTIGATION INTO THE REDOX CONDITIONS OF A LANDFILL LEACHATE PLUME CONTAINING VOLATILE ORGANICS, GLOUCESTER, ONTARIO** .... L. Elliott, J. Develin, F. Michaels and W. Gorman, Queen's University, Kingston, Ontario.	64
67	**EFFECTS OF INCREASING AMOUNTS OF NON-POLAR ORGANIC LIQUIDS IN DOMESTIC WASTE LEACHATE ON THE HYDRAULIC CONDUCTIVITY OF CLAY LINERS IN SOUTHWESTERN ONTARIO** .... R.M. Quigley and F. Fernandez, University of Western Ontario, London, Ontario.	65
68	**ASSESSMENT OF CONTAMINANT MIGRATION FROM INDUSTRIAL SOURCES DISCHARGING TO THE WELLAND RIVER** .... M. Dickman and I. Brindle, Brock University, St. Catherines, Ontario.	66
69	**EVALUATION OF CONTAMINANT VELOCITY GROUNDWATER IN LOW PERMEABILITY FRACTURE SHALE** .... E. Sudicky, R. Blackport and J. Cherry, University of Waterloo, Waterloo, Ontario.	67

Paper No. **Page No.**

70 **GEOMECHANICAL INVESTIGATION OF NEAR-SURFACE FRACTURES IN CLAY TILLS** 68
M. Dusseault and A.Vorauer, University of Waterloo, Waterloo, Ontario.

71 **ORIGINS OF ELEVATED CHLORIDE CONCENTRATIONS IN GROUNDWATER SYSTEMS** 69
P.E. Pilon and K.W.F. Howard, University of Toronto, Scarborough, Ontario.

SESSION D: ANALYTICAL METHODS

FEATURE PAPERS

A **TRENDS IN MULTI-ELEMENT ANALYSIS: THE ROLE OF ICP-MS IN ENVIRONMENTAL APPLICATIONS** 71
Barry French, Institute for Aerospace Studies, University of Toronto, Toronto, Ontario, Canada.

B **DETECTION OF HYDROXYLATED NITRO-POLYNUCLEAR AROMATIC HYDROCARBONS AND KETONES IN AN AMBIENT AIR PARTICULATE EXTRACT USING BIOASSAY-DIRECTED FRACTIONATION** 72
Marcia G. Nishioka and Corrine C. Howard, Analytical Chemistry Section, Battelle Columbus Division, Columbus, Ohio, and Joellen Lewtas, U.S. - EPA, North Carolina, U.S.A.

SESSION PAPERS

28 **DIRECT SOLID SAMPLE ANALYSIS WITH THE DIRECT SAMPLE INSERTION DEVICE, PROMISE AND PROBLEMS** 73
E. Salin and R.L. Sing, McGill University, Montreal, Quebec.

29 **SCREENING METHODS FOR AIR AND WATER SAMPLES: APPLICATION OF INDUCTIVELY COUPLED PLASMA MASS SPECTROMETRY (ICP/MS) TO ELEMENTAL ANALYSIS** 74
J. Van Loon and B.French, University of Toronto, Toronto, Ontario.

30 **DEVELOPMENT OF SELENIUM ANALYSIS METHODOLOGY AT NG/L LEVELS FOR SOFT WATERS SUBJECT TO ACIDIC PRECIPITATION** 75
L.M. Brown and J. Wehr, University of Western Ontario, London, Ontario.

31 **EVALUATION AND OPTIMIZATION OF A TOC ANALYZER USING UV - PERSULPHATE DIGESTION** 76
R.D. Evans, Trent University, Peterborough, Ontario.

Paper No.		Page No.
32	**DEVELOPMENT OF AN ULTRASONIC NEBULIZER FOR STABLE AND REPRODUCTIVE PRODUCTION OF AEROSOLS FOR ATOMIC SPECTROMETRIC ANALYSIS**................. J.C. Van Loon, University of Toronto, Toronto, Ontario.	77
33	**DEVELOPMENT OF RECOMBINANT DNA PROBES TO DETERMINE THE ORIGIN OF FECAL STREPTOCOCCI AT THE TORONTO AREA BEACHES**....................... W.C. Bradbury, M.A. Marko, L. Papageorgiou, D. Leight and D. Rego, University of Toronto, Toronto, Ontario.	78
34	**PLANT BIOASSAYS FOR THE DETECTION OF ENVIRONMENTAL MUTAGENS**........................ Wm. F. Grant, McGill University, Montréal, Quebéc.	79
35	**A BIOLOGICAL INDICATOR SYSTEM TO IDENTIFY GENOTOXICITY OF IN-PLACE POLLUTANTS**............... D.R. Hart, J. Fichko, M. Brinkman and P. McKee, IEC Beak Consultants Ltd., Mississauga, Ontario.	80
36	**FRESHWATER CLAMS AS MONITORS OF VARIATION IN ENVIRONMENTAL ACIDITY AND TRACE METAL LEVELS**...... R.H. Green, S. Hinch and R. Bailey, University of Western Ontario, London, Ontario.	81
72	**ANALYSIS OF DIOXINS AND FURANS IN FISH AND OTHER BIOTA**............................ F.W. Karasek, T. Thompson, D. Schelenberg and K. Naikwadi, University of Waterloo, Ontario.	82
73	**DEVELOPMENT OF COST-EFFECTIVE PROTOCOL FOR ROUTINE ANALYSIS FOR TRACE ORGANIC CONTAMINANTS IN MUNICIPAL WPCP RAW SEWAGE AND FINAL EFFLUENT**................................. C. Chan[1], J. Martin[1], P. Pond[1], G. Rees[2], and T. Ho[2]. 1-Mann Testing Labs. Ltd., 2-Environment Ontario.	83
74	**APPLICATION OF GC HELIUM MICROWAVE PLASMA DETECTION TO THE RAPID SCREENING OF CHEMICAL WASTE**................................. M. Danszinger, Barringer Magenta Ltd., Rexdale, Ontario.	84
75	**DEVELOPMENT OF METHODS SUITABLE FOR THE USE IN THE AMES SALMONELLA MUTAGENICITY ASSAY FOR THE COLLECTION OF ORGANICS PRESENT IN GROUNDWATER AND LANDFILL SITE MATRIX MAERIALS**................ G.H. Thomas, A. Horton and K. Matsummura, Ontario Research Foundation, Mississauga, Ontario.	85

Paper No. **Page No.**

76 **SYNTHESIS OF OXYGEN AND SULPHUR PAHS**
OF INTEREST IN ENVIRONMENTAL POLLUTION 86
E. Lee-Ruff and F. Ablenas, York University,
Toronto, Ontario.

77 **DEVELOPMENT OF A ROBOTIC WORKSTATION FOR THE**
ROUTINE ANALYSIS OF ORGANICS IN BIOLOGICAL
TISSUES USING ACID DIGESTION AND SOLVENT
EXTRACTION METHOD 87
C. Chan[1], J. Martin[1], G.Ladwig[1], G. Rees[2], and
G. Crawford[2]. 1-Mann Testing Labs Ltd.,
2-Environment Ontario.

78 **SEPARATION AND IDENTIFICATION OF ORGANIC**
COMPOUNDS IN EXTRACTS OF AIR PARTICULATES
BY HPLC AND GC/MS 88
K.P. Naikwadi, G. Charbonneau and F.W. Karasek,
University of Waterloo, Waterloo, Ontario.

79 **QUANTITATIVE DETERMINATION OF SELECTED PAHS'**
BY SHPOL'SKII AND JET-COOLED SPECTROSCOPY 89
C.M. Sadowski, J. Lai, H. Malle, S. Filseth and
F. Morgan, York University, Toronto, Ontario.

80 **NEW SYNTHETIC METHODOLOGY FOR THE EXPEDIENT**
PROVISION OF PURE PAH ANALYTICAL STANDARDS 90
V.A. Snieckus, University of Waterloo,
Waterloo, Ontario.

SESSION E: ENVIRONMENTAL ECONOMICS

FEATURE PAPER

A **THE ENVIRONMENT OF ECONOMICS - PAST PRESENT**
AND FUTURE ROLES OF ECONOMICS IN ENVIRONMENTAL
MANAGEMENT 92
Clifford Russell, Director, Institute for Public
Policy Studies, Vanderbilt University,
Nashville, Tennesee, U.S.A.

SESSION PAPERS

37 **ABATEMENT COST FUNCTIONS - THE WORKHORSE**
OF ENVIRONMENTAL MANAGEMENT 93
J. Donnan, C. Griffith, S. Glover and M. Dandele,
Policy & Planning Branch, Ministry of the
Environment, Toronto, Ontario.

38 **MEASURING THE SOCIAL COSTS OF ELECTRICAL**
EXPORTS AND COST RECOVERY OPPORTUNITIES OF
ENVIRONMENTAL PROTECTION OF ONTARIO HYDRO 94
W. Wianko and B. Green, Ontario Hydro, Toronto,
Ontario.

Paper No.		Page No.
39	**QUÉBEC'S EXPERIENCE WITH THE ECONOMIC EVALUATION OF ENVIRONMENTAL REGULATIONS - WHAT LESSONS HAVE BEEN LEARNED** .... C. Sauvé, Ministére de l'Environment, Sainte-Foy, Québec.	95 & 96
40	**3M'S POLLUTION PREVENTION PAYS PROGRAM** .... A.G. Mills, 3M Canada Inc., London, Ontario.	97
41	**THE BENEFITS OF REDUCING LEAD IN U.S. DRINKING WATER** .... R. Levin, U.S.-EPA, Washington, D.C., U.S.A.	98
42	**ECONOMIC EFFECTS OF REDUCED FOREST GROWTH IN THE UNITED STATES' FOREST ECONOMY AND ON CANADIAN-U.S. LUMBER TRADE** .... J.M. Callaway, Jr., Battelle Northwest Labs, Richland, Washington, U.S.A.	99
43	**SOME ECONOMICS OF THE GRAND CANAL** .... A. Muller, Department of Economics, McMaster University, Hamilton, Ontario.	100

KEYNOTE PAPERS

ABSTRACT FORM

Author : Gabriel L. Plaa
Address : Faculty of Medicine, University of Montreal
Quebec, H3C 3J7 Phone (514) 343-6300
Co-Authors :

Topic Area : Air ☐, Water ☐, Waste ☐, Analytical ☐
Environmental Economics ☐

Do you prefer presenting: A paper ☒, a poster session ☐

Title: Crucial Issues in Environmental Toxicology

Abstract:

An overview on Environmental Toxicology will be presented including:

- the study of adverse effects of contaminants in air, water and soil;
- the biological targets of these chemicals including humans;
- subdivision of environmental toxicology; and
- toxicological assessment.

The dose-effect and dose-response relationships will also be discussed with emphasis made on the distinction between "toxicity" and "hazard" as well as exposure assessment.

Problems associated with chemical analyses, bioavailability, bioaccumulation, biotransformation relative to the chemical half-life and its translocation in air, water and soil will be summarized.

The review will also cover the climate of confrontation and adversal posturing, the problems associated with scientific credibility and the responsibility for the solution of the pressing toxicological issues.

ABSTRACT FORM

Author : E.F. Roots
Address : Environment Canada, Ottawa, Ontario, K1A OH3
Phone (819) 997-2393
Co-Authors :

Topic Area : Air ☐, Water ☐, Waste ☐, Analytical ☐

Environmental Economics ☐

Do you prefer presenting: A paper ☒, a poster session ☐

Title: Some International Developments in Environmental Aspects of Industrial and Technological Activities

Abstract:

Recent international developments reflect the increasing importance of environmental factors in economic activities and can be expected to affect industrial enterprises and technological development in Canada and other countries. In 1984, the Heads of State of the seven Economic Summit countries - Canada, France, Italy, Japan, U.K., U.S.A., West Germany - and the European Economic Community recognized the importance of environmental quality to economic prosperity. They instructed the Working Group on Technology, Growth and Employment (TGE) to review areas where environmental factors were most important to future economic development, and to make recommendations for international and industrial action.

In its report to the 1985 Economic Summit in Bonn, the TGE identified major areas where environmental conditions have a significant present or potential influence on technology, economic performance or employment. It recommended policy actions to being environmental management into industrial practices, and identified 62 subjects where additional research or development of environmental control measures or technologies as needed, in six main categories of environmental concern: air pollution, toxic and hazardous wastes, pollution of streams and groundwaters, marine pollution, inappropriate land husbandry, and climate change. It also noted that there was an important need for improvement and international harmonization of the techniques and practices of environmental measurement, so that environmental data could become more reliable and comparable, and to avoid environmental issues becoming unjustified factors in international trade because of incompatible information.

The TGE Environment Group has further studied this problem. Together with international scientific bodies it has developed general principles for environmental measurement and identified specific subject areas where improved scientific understanding or technique development is needed, and areas where improved management of environmental information is needed. A progress report was accepted by the 1986 Economic Summit in Tokyo and the Group is now preparing, for presentation to the 1987 Summit in Rome, a proposal for an on-going mechanics, under the authority of an established international organization, for achieving continuing improvement of environmental data in ways that are relevant to new technologies and industrial processes.

(continued).....

At the same time, the International Council of Scientific Unions' Committee on Data for Science and Technology (CODATA) has become concerned about the shaky scientific basis of much environmental data. The first CODATA workshop on environmental data was convened in Montreal in May 1986, "Directions for Internationally Compatible Environmental Data", with representatives from 19 countries and 32 different national or international standards or scientific data organizations. The workshop identified areas of weakness or incompatibility in basic data or measurements pertaining to air, water, and soil, and explored environmental data management needs on various scales for different uses: global understanding, regional management, regulatory, and environmental assessment.

These two developments, together with the evolution of the World Data Centres whose role was re-examined at the ICSU General Assembly at Berne in September 1986 mark important progress, supported at the highest political and scientific level, in the fundamental questions of measuring the characteristics of the environment and the setting of environmental standards. Their effects may be expected to influence nearly every laboratory or industrial process that uses natural resources or has an effect on the environment.

ABSTRACT FORM

Author : James W. Falco
Address : Office of Environmental Processes and Effects Research
Washington, D.C. 20460 Phone ( )
Co-Authors :

Topic Area : Air ☐, Water ☐, Waste ☐, Analytical ☐

Environmental Economics ☐

Do you prefer presenting: A paper ☒, a poster session ☐

Title: The United States Environmental Protection Agency's Program to Evaluate the Effects of Toxic Chemicals

Abstract:

The United States Environmental Protection agency conducts an extensive research program related to the control and evaluation of toxic substances. The Office of Environmental Processes and Effects Research is responsible for conducting the portion of this research which deals with the evaluation of toxics substances. Among its major programs, several shifts in research emphasis are taking place. First, there is a shift from development of methods which yield a single valued estimate of ecological effects. Secondly, increased emphasis is being placed on evaluating local ecological problems in addition to regional and national problems.

The Agency is currently emphasizing ecological effects research in 6 major areas: groundwater, biotechnology, wetlands, ecological risk assessment, acid deposition, and Great Lakes research.

SESSION A

AIR QUALITY RESEARCH

ABSTRACT FORM

Author : H.P. Sims

Address : Research Management Division, Alberta Environment,
Edmonton, Alberta Phone (403) 427-3096

Co-Authors : G.A. Singleton and H.S. Sandhu

Topic Area : Air ☒, Water ☐, Waste ☐, Analytical ☐

Environmental Economics ☐

Do you prefer presenting: A paper ☒, a poster session ☐

Title: An Overview of Alberta Environment's Deposition Program

Abstract:

Relative to Alberta, our knowledge regarding medium and long-range transport of air pollutants/acid rain and the biological effects of long-term, low-level emissions is presently limited. Some concerns are: (a) the acidification of surface waters and the potential consequences for aquatic biota, including fish; (b) acidification of soils and their influence on the total watershed, vegetation and aquatic systems; (c) direct effects on agricultural crops and forest tree species; and (d) direct and indirect effects on human and animal health.

Alberta Environment established a Departmental Acid Deposition Research Program comprised of four distinct but integrated components:

1. Alberta Environment's acid deposition research program to address the environmental impacts of oil sands development in northeastern Alberta on forest and aquatic ecosystems.
2. The Alberta Government/Industry Acid Deposition Research Program, focused primarily on agriculture and human health.
3. Western and Northern Canada LRTAP federal/interprovincial program (Long Range Transportation of Air Pollutants).
4. Monitoring of acid forming emissions and other pollutants.

The program will provide scientific information for evaluating and reviewing Alberta's current air quality standards, emission guidelines, and regulatory controls with respect to socio-economic and environmental consequences of atmospheric pollutants.

Earlier acid-deposition research demonstrated clearly the high degree of variability in the measurement of ecosystem parameters in forested systems and the difficulty with measurement of the effects of low concentrations of pollutants. It has become clear in recent reviews that a new strategy is required for evaluation of acid deposition effects. This strategy will be to develop biomonitoring indices that will be used to monitor effects of low levels of acid forming emissions over the long term.

As well the research program will undertake studies to determine the capacity of the ecosystem to resist detrimental effects. Work will be undertaken on control technologies to reduce emissions at their source.

The Alberta Environmental Centre is undertaking a study on the health effects of sulphur gases. The objective is to determine the effects of toxic or potentially toxic gases, vapours, particulates, and aerosols on animals and, by extrapolation, on humans.

ABSTRACT FORM

Author : Ronald Harkov
Address : New Jersey Department of Environmental Protection, Trenton
New Jersey, 08625, USA Phone (609) 984-2207
Co-Authors :

Topic Area : Air ☒, Water ☐, Waste ☐, Analytical ☐
Environmental Economics ☐

Do you prefer presenting: A paper ☒, a poster session ☐

Title: Multimedia Analysis and Assessment of Environmental Toxic Carcinogenic Substances: The Regulatory Connection.

Abstract:

Most toxic substance issues are multimedia in nature, but are managed within regulatory agencies as completely separate items. In New Jersey, the Office of Science & Research (OSR) has been involved in multimedia toxic substance assessments of air, water, food and soil contamination. These efforts have led to one of the best toxic substances inventories in the US, and perhaps the most far-reaching program of its kind at the state level. The research described in this report sets the foundation for development of an integrated toxic substances program. While volatile organic compounds (VOC) are used for illustration purposes, it is clear that multimedia analysis of human toxic substance exposures will be needed to develop cost-effective environmental solutions. To this end a new environmental health office is being initiated within OSR to address: risk assessment, risk reduction and risk communication aspects of a toxic substance regulatory program.

ABSTRACT FORM

Author : Bori. I. Shushan
Address : SCIEX, 55 Glen Cameron Road, #202,
Thornhill, Ontario Phone (416) 881-4646
Co-Authors : Angie Ngo, V. Ozvacic, G. Wong, G. DeBrou, B. Bobbie,
R.E. Clement, S.J. Thorndyle and B. Chittum

Topic Area : Air ☒, Water ☐, Waste ☐, Analytical ☐
Environmental Economics ☐

Do you prefer presenting: A paper ☒, a poster session ☐

Title: The Rapid Screening of Municipal Refuse Incinerator Fly-Ash and Stack Gas for PCDD/PCDF Using a Transportable Tandem Mass Spectrometer (GC/MS/MS) System.

Abstract:

The formation of polychlorinated dibenzo-p-dioxins and dibenzofurans (PCDD/PCDF) is strongly linked to the incineration of municipal refuse. To date, there has been no study which demonstrated clearly what, if any, incinerator operation parameter(s) this production correlates with. Part of the problem in determining such correlations is that testing for PCDD/PCDF is an expensive and time-consuming effort. This paper describes a rapid analytical approach using gas chromatography (GC) coupled to tandem triple quadrupole mass spectrometry (MS/MS). This combination has been demonstrated to be more specific conventional GC/MS while requiring less time per analysis. Furthermore, the instrument used in the present work (The TAGA 6000E manufactured by SCIEX) is fully transportable, permitting it to be driven to the incinerator for rapid on-site PCDD/PCDF analysis. The analysis of fly-ash and stack gas will be described and analytical results compared to GC/MS analyses performed on the same samples.

ABSTRACT FORM

Author : R.W. Nicholls
Address : Centre for Research in Experimental Space Science,
York University Phone (416) 736-5247
Co-Authors : M. Amani, M. Mandelman and W.H. Morrow

Topic Area : Air ☒, Water ☐, Waste ☐, Analytical ☐

Environmental Economics ☐

Do you prefer presenting: A paper ☒, a poster session ☐

Title: Retrospective Correlation Spectroscopy and its Application to Atmospheric Monitoring.

Abstract:

Correlation spectroscopy is a diagnostic procedure for determination of column densities of absorbers by quantitative correlative comparison between the spectral signatures of a field spectrum and the intrinsic spectral features of such molecular species of interest as oxides of sulphur and nitrogen. Dispersive and non-dispersive correlation methods have been developed. In the past, analogue applications of these methods have been developed. In this paper a review is given of newly developed digital methods of dispersive and non-dispersive correlation spectroscopy.

In retrospective correlation spectroscopy the traditional oscillating focal plane mask, which is the mechanical analogue of the molecular species spectrum, is replaced by a numerical digitally synthesised mask for each species of interest. Correlations between the digitally recorded field spectrum and each mask are retrospectively evaluated digitally. From a theoretical assessment of the method in optically thin cases, it is easy to show that

$$C(z) = A - NX\,E(z)$$

where $C(z)$ is the correlation integral between the field spectrum and mask function when out of register by an amount z, A is the mask area, and $E(z)$ is the convolution of the mask function with the absorption cross-section function of the spectral feature in question. $C(z)$ and $E(z)$ can be numerically evaluated for each of a range of values of z. This equation provides a direct diagnostic method of evaluating the column density NX of the species over a path X for a concentration N from the slope of a plot of $C(z)$ vs. $E(z)$. This method has been tested by using digitally recorded sulphur dioxide spectral features and a variety of mask and absorption cross section functions of increasing realism. A very full quantitative examination of the results has been made, and the usefulness of the above diagnostic equation has been confirmed.

In a related study, supported by NSERC, two digital gas filter non-dispersive correlation spectrometers, GASCOFIL and GASCOSCAN have been developed for remote sensing of trace atmospheric species. These instruments operate over a spectral range from the ultra-violet to the near infrared. Their design, operating characteristics and performance in field tests will be described.

ABSTRACT FORM

Author : H.I. Schiff
Address : 222 Snidercroft Road, Concord, Ontario,
L4K 1B5 Phone (416) 669-2280
Co-Authors :

Topic Area : Air |x|, Water | |, Waste | |, Analytical | |

Environmental Economics | |

Do you prefer presenting: A paper |x|, a poster session | |

Title: Measurements of Atmospheric Constituents By Tunable Diode Laser Absorption Spectrometry.

Abstract:

Tunable diode laser absorption spectrometry (TDLAS) operating in the 5 to 10 micron region affords a number of advantages for measuring these species. It is a universal method applicable, in principal, to any gas of atmospheric interest. Because of its high resolution, it provides positive identification with no interferences from other gases. By utilizing the long path length of a White cell it can detect most molecules at concentrations found in the atmosphere. It is a passive technique which can provide real time, in situ measurements, with a time resolution better than 1 min.

The application of the method to measurement of trace atmospheric constituents has three requirements: (1) the selection of an appropriate absorption line which usually involves a compromise between the line strength of the absorber and the operating characteristics of the diode, (2) the development of a calibration procedure for the target gas and (3) the development of procedures to ensure sampling integrity and tests to assure linearity between absorption signal and concentration of the target gas in the sampled air.

A field instrument which meets these requirements for NO, NO_2 and HNO_3 has been described by Schiff et al (1). Calibration and sampling procedures have subsequently been developed for SO_2, HCHO, H_2O_2 and NH_3.

A second laser head assembly was subsequently added to the system to permit a number of gases to be measured simultaneously. Further modifications included the incorporation of computer controlled operation and data acquisition and processing systems. Considerable improvements in background stability and, consequently, in detection limits was achieved by using temperature rather than current controlled line locking.

The modified system was used in a number of field missions and proved to have adequate sensitivity to measure most atmospheric species in rural and urban air. Additional sensitivity was required, however, to measure H_2O_2 during most of the year and the other gases in very clean air. A modified White cell and associated optics has been incorporated in the system and shown to provide detection limits of these gases of less than 100- pptv.

This upgraded system has also flow on an aircraft to sample oceanic and continental air in and above the planetary boundary layer.

References: (1) Schiff, H.I., Hastie, D.R., MacKay, G.I., Iguchi, T and Ridley, B.A., Envir. Sci. Technol., 17 352A (1983).

ABSTRACT FORM

Author : W.J. Megaw
Address : York Univesity, 4700 Keele Street, North York
Ontario, M3J 1P3 Phone (416) 736-2100
Co-Authors : J.F. Hicks

Topic Area : Air ☒, Water ☐, Waste ☐, Analytical ☐

Environmental Economics ☐

Do you prefer presenting: A paper ☒, a poster session ☐

Title: Uptake, Distribution, and Clearance of Soluble Aerosols in the Human Respiratory System.

Abstract:

In humid atmospheres, soluble aerosols may grow in size as water condenses on the particle surfaces. The growth of soluble aerosols in the humid environment of the respiratory tract will affect the degree and site of deposition in the lungs. Since most of the ambient aerosol is hygroscopic, this has a direct bearing on the estimation of health effects due to air pollution. This study investigated the growth, deposition, and clearance of soluble aerosols in the human respiratory system.

Using a radioactive tracer, the study assessed the deposition of soluble aerosols when inhaled by a number of volunteers. Contrary to theory, most of the particulate deposited in the conducting airways of the lung. Furthermore, major pathways of aerosol clearance from the respiratory tract were traced. Two mechanisms, absorption in to the body fluids and mucocillairy clearance, were most important in removing soluble aerosol contaminants from the respiratory system.

ABSTRACT FORM

Author : John A. Heddle
Address : Deparment of Biology, York University, Toronto
Ontario, M3J 1P3 Phone (416) 736-2100 (3053)
Co-Authors : A. Bouch, D.B. Couch, H.K. Kaul, J.D. Gingerich, K. Jain

Topic Area : Air ☒, Water ☐, Waste ☐, Analytical ☐
Environmental Economics ☐

Do you prefer presenting: A paper ☒, a poster session ☐

Title: Experimentally Determined Mutation Rates in Lung as an Air Quality Standard.

Abstract:

A quantitative assay for the toxic effect of air-borne contaminants that is both relevant and inexpensive would be useful in establishing air quality standards. We are developing such an assay for carcinogenic air pollutants based on measurements of mutation in lung cells and tracheal cells in test animals.

Two approaches have been tried. The first is to assay mutations in the target cells themselves. Since these cells cannot be cloned quantitatively, traditional mutation measurements, which are based on cloning, are not feasible. Instead we have been using autoradiography to detect mutants resistant to diphtheria toxin, an agent that specifically inhibits protein synthesis. Since resistant mutants will continue to synthesize protein after exposure to the toxin, but normal cells will not, only the mutants will incorporate tritiated leucine and so be labelled. With this assay we have found reproduceable but small increases, approximately three-fold, in the frequency of mutant cells in Chinese hamsters exposed to urethane, a known lung carcinogen and to ethylnitrosourea, a catholic mutagen. These results make it clear that the optimal conditions for detecting mutants in the lung cells have not yet been found.

A second approach has been to culture the fibroblasts that are in close association with the target cells throughout the lung and measure the frequency of mutants resistant to azaguanine in them by the colony-forming technique. This assay demonstrated a dramatic and reproduceable increase in the frequency of mutants following in vivo exposures of the hamsters to ethyl methane sulphonate and diethylnitrosamine. This exciting finding is being very actively pursued to determine whether or not specific pulmonary carcinogens are also detected rapidly and easily. The results obtained with several such chemicals will be reported together with progress towards optimizing the autoradiographic assay.

ABSTRACT FORM

Author : L.D. Pengelly
Address : Room 3E27, Health Sciences Centre, McMaster University
120 Main W. Hamilton Phone (416) 525-9140 X2720
Co-Authors : A.t. Kerigan, C.H. Goldsmith, W. Furlong, S.A. Toplack

Topic Area : Air ☒, Water ☐, Waste ☐, Analytical ☐
Environmental Economics ☐

Do you prefer presenting: A paper ☒, a poster session ☐

Title: The Hamilton Study: Effect of Fine Particles on the Respiratory Health of School Children.

Abstract:

Hamilton, Ontario, is an industrial city with a population of 300,000 situated at the western end of Lake Ontario. The level of particle pollution has historically been high, a portion of which has been attributed to the activities of Canada's two largest iron and steel mills located here. Although in the last two decades air quality has improved markedly, there has been a continuing community concern about the effects of air pollution on health. From 1979 to 1982, we carried out an epidemiological study of the respiratory health of a cohort of over 3500 elementary school children in whom we also determined the extent to which they were exposed to ambient particles of different sizes. Respiratory health was assessed by determining each child's respiratory symptoms and health history using a questionnaire administered to the parents. In addition, comprehensive tests of pulmonary function were carried out on the children at their schools. Particle size and concentration were measured using two networks: one of 7 to 9 Andersen 2000 cascade impactors, and another of 27 GMW Hi-Vol TSP samplers. Both networks were distributed over the area of the city. Other environmental factors thought to "confound" the relationship between respiratory health and air pollution were also examined, via information collected in the parental questionnaire; e.g. parental smoking, use of gas for cooking, socio-economic status. Results of a cross-sectional analysis of the data from the cohort in the second year of the study showed a strong effect of maternal smoking on the prevalence of cough and bronchitis, with little air pollution effect on these variables. Two pulmonary function variables, peak flow (adjusted for height) and maximum expiratory flow at 75% VC (adjusted for height) showed an association with the presence of fine particles.

ABSTRACT FORM

Author : M.L. Petras
Address : Department of Biological Science, University of Windsor
Phone (519)253-4232
Co-Authors : J. Norsworthy, M. Vrzoc and K. Hill

Topic Area : Air ☒, Water ☐, Waste ☐, Analytical ☐
Environmental Economics ☐

Do you prefer presenting: A paper ☒, a poster session ☐

Title: Biological Monitoring of Environmental Genotoxicity.

Abstract:

The SISTER CHROMATID EXCHANGE (SCE) assay has been modified so that wild mice can routinely be used to monitor the environment for general genotoxicity. The use of bromodeoxyuridine tablets and improvement of the staining procedure have permitted the processing of an adequate-sized sample (30 mice or more) at one time with consistently good results. This procedure has now been applied to wild mice collected from a number of localities in southwestern Ontario over the last three years. The annual temporal and geographic patterns have been similar from year to year. The SCE values/mouse are low in the early spring (prior to the spraying of crops with pesticides), high in the late spring (spraying period) and generally low in the summer (post-spraying period). The geographic pattern involves high SCE values in mice captured in the western part of the study area (Essex County) and lower values in those from the eastern section (Kent and Elgin Counties). Also we have examined the effects of a number of factors on SCE levels and their variability. These have included: short-term stress, age, genetic heterogeneity, some commonly used herbicides, several chemicals encountered in the plastics-molding industry and fumes in a diesel garage. Only chromic acid (plastics-molding industry) and diesel fumes significantly increased SCE values.

The MICRONUCLEUS ASSAY OF PERIPHERAL BLOOD was selected as a back-up system to permit corroboration of the SCE results. This assay was chosen because: 1) with fluorescence microscopy the typing of micronucleated cells is very straightforward and can be done rapidly, 2) the mouse is not sacrificed and blood samples from the same animal can be obtained at different times after treatment, 3) no pretreatment of animals is necessary prior to obtaining testable blood samples, and 4) a single recent (within 72 hours) exposure of an animal to a genotoxic agent can be distinguished from both an earlier exposure and chronic exposure. Furthermore, although most agents induce both SCEs and micronuclei there are some that cause the latter but not the former making the two tests complementary. So far a time-response curve has been developed for two compounds, cyclophosphamide and mitomycin C. Peak induction of micronuclei occurs at around 48 hours after injection of either agent. This appears to be about 12 hours later than induction of micronuclei in bone marrow cells. The micronucleus assay has been applied to wild mice being examined for SCE's as well as mice being used in several experimental situations.

The results of both tests will be presented, compared and discussed in detail.

(This reasearch is supported by a grant from the Ontario Ministry of the Environment).

ABSTRACT FORM

Author : C.S. Davis
Address : Concord Scientific Corporation, 2 Tippett Road
Downsview, M3H 2V2 Phone (416) 630-6331
Co-Authors : S.G. Guerin, J. Marr*, M. Quilliam* (*McMaster University)

Topic Area : Air ☒, Water ☐, Waste ☐, Analytical ☐

Environmental Economics ☐

Do you prefer presenting: A paper ☒, a poster session ☐

Title: Field and Laboratory Validation of a HiVol Denuder for Minimizing PAH Oxidant Reactions.

Abstract:

Results of a recent study: "Evaluation of Alternatives to HiVol Sampling for Polynuclear Aromatic Hydrocarbons", by Concord Scientific Corporation for the Air Resources Branch, showed that a denuder efficiently removes ozone from an air stream prior to a HiVol filter. In a single experiment, the ozone denuder appeared to reduce on-filter reactions between ozone and captured PAH, as indicated by the significant drop in the number of oxy-PAH species in a protected filter compared to an unprotected filter. Additional verification of the efficiency of the denuder-HiV1 system in reducing or eliminating reactions of collected PAH with ozone and other species (HNO_3) removed by the denuder was therefore required.

The objective of this study was to evaluate further the HiVol ozone denuder in terms of mass collection and the relative attenuation of PAH and PAH derivatives, the effectiveness for removal of NO_2 and HNO_3, and the identification of the oxy- and nitro-PAH contained in the extract of the denuder filter compared to a standard HiVol filter and to determine the lifetime of the denuder bundle. The primary purpose of the program was to identify the chemical species present on the protected versus standard filter and thus determine the effect, if any, of the denuder. Field and laboratory tests were to be performed.

The experimental data from this study have shown the following:

1. The denuder is effective not only for ozone, but also for nitric acid. Break-through of HNO_3 was found to occur only after 16,500 ppb-h exposure. The estimated lifetime respecting nitric acid would be about 70 days continuous operation. Within these limits, the removal efficiency for HNO_3 was $>99\%$ at room temperature and $>85\%$ at 0°C.
2. After 42 days continuous field operation with a mean ozone concentration of 22ppb, the denuder's efficiency for removing ozone was 85% for a laboratory ozone challenge concentration of 155 ppb and 90% removal efficiency for 50 ppb.
3. Similar particle catches for the standard HiVol and a denuder HiVol were obtained in two of three tests. In the third test the particle catches for denuder HiVol was lower (by $\sim$ 22%). Earlier tests had shown about 15% mass attenuation.
4. Analysis of extracts from standard and denuder HiVol field samples showed insignificant differences in the PAH derivative composition.
5. Laboratory tests showed that the denuder reduced the formation of oxygenated PAH derivatives within fairly broad analytical uncertainty.
6. Dynamic laboratory tests in which preloaded filters were challenged with nitric acid showed no differences in the PAH derivative fractions between samples.
7. Analogous tests on filters using static chamber exposure conditions for O_3, and HNO_3 and NO_2 separately showed no differences in the PAH derivative fraction compared to control filter.

Based on these results, the contemplated use of a denuder HiVol in a network would be justified only respecting protection provided by the removal of ozone.

ABSTRACT FORM

Author : R.E. Jervis
Address : Dept. of Chemical Eng. and Applied Chemistry
University of Toronto Phone (416) 978-3071
Co-Authors : T.G. Pringle

Topic Area : Air ☒, Water ☐, Waste ☐, Analytical ☐
Environmental Economics ☐

Do you prefer presenting: A paper ☒, a poster session ☐

Title: A Particle-Size-Specific Elemental Mass Balance for Apportionment of Ambient Aerosol Sampled with Multistage Fractionators

Abstract:

Receptor models for aerosol-emission source apportionment have received increasing attention during the past decade. However, the usual elemental models are often limited in their application and development especially in situations where there are several aerosol sources which have somewhat similar elemental microcomposition. A judicious use both of particle-size sampling and multi-elemental concentration measurements in a modified receptor model, for which we have defined the term "particle-size specific elemental mass balance, SSEMB" can facilitate the distinguishing of such similar sources. This has been demonstrated in this current research project - as detailed below.

The applied radioanalytical methods of instrumental photon and thermal-neutron activation analysis (INAA) have been adapted to determine total elemental concentrations of up to thirty chemical elements (including Al,As,Ba,Br,Ca,Cr,Fe,Mn,Na,Ni,Pb,Sb,Sc,Se, Ti,U,V and Zn) in six particle-size fractions of urban airborne particulate matter collected by Sierra cascade impactor. Both these analytical techniques are multi-elemental in nature, quite sensitive and reasonably non-destructive: all desirable attributes of methods for aerosol analysis given the small mass of material in each size fraction collected and, also, the need to achieve sufficiently low analytical variance to permit subsequent statistical modelling based on the multi-component concentration data obtained.

Hi-Volume air samplers fitted both with Anderson and Sierra 235 cascade impactor heads were used with coated cellulose substrates to partition urban air-borne particulate matter into 5 or 6 size fractions during typical 12 hour sampling periods at three locations in greater Toronto: Port Credit, Toronto Island and Eastern Avenue. Characterization of the material collected on the several impactor sages was performed by scanning electron microscopy.

Contrary to previous published reports (1), the cellulose substrates used with these impactors did not cause marked distortion of the stage-by-stage collection characteristics of the impactor as both scanning electron micorphotographs and INAA performed on portions of vaseline substrate indicated a dramatic reduction in particle bounce-off from stage to stage. Considering this and the larger number of size fractions yielded by the Sierra unit when compared to the more widely-used dichotomous samplers, the value of our aerosol sizing method is clearly demonstrated.

(continued)

The particular-size distributions obtained in these studies of air particulates from the greater metropolitan Toronto region, such as the distributions of Al,As,Ca,Br,Mn,Pb, V and Zn revealed varying effects of both natural and anthropogenic sources of aerosol. While the majority of the elements studied exhibited particle-size distributions shifted either to mainly large (eg. Al,Sc,Zr) or mainly small particles (e.g. Br,Cl,Cu) which can be taken as generally indicative of physical ablation or high temperature combustion sources, respectively, the size distributions of several other elements (viz. Pb,Zn,As,Sb) exhibited different and unusual shapes in several sets of air particulate samples. Such unusual distributions were identified at a site near a lead smelter, incinerator and motorway where Pb sources ranged from fine particles from vehicle exhaust and variably-sized industrial emissions. These were used in a novel SSEMB model to aid in the accurate apportionment of aerosol among the colinear contributing sources involved.

References:

1. H. Sievering, M. Dave, P.McCoy, K. Walter, Environ. Sci. Tchnol., 12 (1978) 1435.

2. K. Willeke, "Performance of the Slotted Impactor", American Industr. Hygiene Assoc. J., Sept. 1975, 683-691.

ABSTRACT FORM

Author : A.S. Raj
Address : CREQ Office, York University, 4700 Keele Street,
North York Phone ( ) 736-2100 ext. 3634
Co-Authors : Morris Katz or 3446

Topic Area : Air ☒, Water ☐, Waste ☐, Analytical ☐

Environmental Economics ☐

Do you prefer presenting: A paper ☒, a poster session ☐

Title: Mutagenicity of Complex Mixtures of Polycyclic Aromatic Hydrocarbons in Ambient Air Particulate Matter

Abstract:

Polycyclic Aromatic Hydrocarbons (PAH) are a particularly important group of carcinogenic pollutants in the atmosphere to which man and animals are exposed. Human exposure to PAH mixtures may produce carcinogenic effects depending on the ratios of the various strong carcinogens to weak - or non-carcinogenic constituents.

We tried to estimate the mutagenicity of the different PAH present in the Standard Reference Material (SRM) 1649 that was purchased from U.S. National Bureau of Standards. 13 PAH have been identified in the SRM 1649 and these are: Phenanthrene, Fluoranthene, Pyrene, Chrysene, Benz (a) Anthracene, Perylene, Benzo (b) Fluoranthene, Benzo (K) Fluoranthene, Benzo (a) Pyrene, Benzo (e) Pyrene, Benzo (ghi) Perylene, Dibenz (a, h) Anthracene and Indeno (1,2,3, -cd) Pyrene.

In vivo bone marrow micronucleus assay has been used as a short-term test to assess the mutagencity of individual PAH as well as mixtures of PAH that are present in SRM 1649.

LD 50/7 of SRM 1649 was found to be 535 mg/kg. No dose-related response was found in terms of number of micronucleated polychromatic erythrocytes with the individual PAH like Benzo (b) fluoranthene, Benzo (k) fluoranthene, and Benzo (ghi) perylene. There was response with the crude extract of SRM 1649, but not dose related. The mammalian assays were carried out with mice.

Some of the preliminary experimental results indicated 70% to 84% of inhibition when two promutagens Ba P and DMBA were employed together. No additive effect was observed when Ba P, DMBA and Benzo (ghi) perylene were employed in a mixture. Studies are in progress and updated results will be presented.

ABSTRACT FORM

Author : Dougals P. Ormrod
Address : University of Guelph, Horticultural Science Dept.
Guelph, Ontario, N1G 2W1Phone (519) 824-4120 x 2728
Co-Authors : Jane M. Petitte

Topic Area : Air ☒, Water ☐, Waste ☐, Analytical ☐
Environmental Economics ☐

Do you prefer presenting: A paper ☒, a poster session ☐

Title: Dose-Response Studies of Gaseous Pollutants of Food Crops.

Abstract:

A long-term dose-response study was conducted in a controlled environment facility using carrot 'Spartan Bonus' plants. Fifteen days old plants were exposed to either 0, 0.06, 0.12, or 0.18 ul l^{-1} of O_3 for 7 h one day each week for a total of 5 weeks. Shoot and root growth analyses were conducted on plants which were harvested one week after each exposure. Leaf area and leaf fresh and dry weights were significantly decreased by the 0.18 treatment after one exposure. Leaf injury was significantly increased by the 0.12 and 0.18 treatments after one week of exposure. Root fresh and dry weights were significantly decreased in the 0.12 and 0.18 treatments after the third week of exposure. By the fifth week of exposure, significant reductions in leaf and root parameters occurred in the 0.12, as well as the 0.18 treatments. No significant changes were detected in dry matter partitioning between the roots and shoots in any of the treatments.

An experiment was performed, using 14 days old tomato plants, to determine changes in plant growth and physiology following exposure to O_3 levels (0, 0.035, 0.070 , and 0.105 ul l^{-1}) below those that normally produce visible leaf injury. Leaf and stem growth parameters, stomatal conductance, and chlorophylls a and b were analyzed 3 days following the 7 h exposure. Neither growth nor chlorophyll was significantly affected by the treatments. However, stomatal conductance in the 0.105 treated plants immediately following the exposure. Three days after the exposure, stomatal conductance was significantly reduced in all the O_3.

Research was conducted to determine if comparisons could be made between indoor and outdoor O_3 responses of several crop species. Seeds of 4 soybean, 2 corn, and 3 wheat cultivars were obtained from the USEPA NCLAN program for indoor experiments. These same cultivars had been grown and subjected to O_3 treatments in open-top field chambers in NCLAN studies. In the present experiment, the seedlings were exposed to 0, 0.06, 0.12, or 0.24 ul l^{-1} of O_3 for one 7 h period in controlled environment facilities. The results suggested that a good comparison could not be made between indoor and outdoor experiments determining the effect of O_3 using these species.

ABSTRACT FORM

Author : T.E. Michaels
Address : Dept. of Crop Science, University of Guelph
Guelph, Ontario Phone (519) 824-4120 Ext. 3392
Co-Authors :

Topic Area : Air ☒, Water ☐, Waste ☐, Analytical ☐
Environmental Economics ☐

Do you prefer presenting: A paper ☒, a poster session ☐

Title: Production of Ozone Insensitive White Bean Varieties

Abstract:

Ozone induced foliar damage of white beans has been estimated to reduce white bean seed yields by 7 to 12 percent in Ontario, and result in a monetary loss of $1,185,000. Previously, this project had identified genotypes of bean, including Gold Crop and French Horticultural Bean, with less sensitivity to ozone than is found in currently registered white bean cultivars. Thirty-five breeding lines were selected from among progeny of crosses between ozone insensitive beans and ozone sensitive registered cultivars based on growth chamber and field performance. These 35 lines and 6 parental check cultivars were screened for ozone sensitivity in growth chambers in Spring, 1986. Fourteen-day-old bean seedlings were exposed to 0.20 ppm ozone for 6 hours each of 4 consecutive days. On day 5, injury of the two unifoliate leaves was rated using the Horsfall-Barratt scale and the Digitized Video Image Analysis System. The DVIA system digitizes the video image of a bean leaf and determines the mean and standard deviation of pixel luminescences for that leaf image. Analysis of variance of the Horsfall-Barratt scores and video image data indicated that breeding line differences were significant. The standard deviation of pixel luminescences was in better agreement with percentage damaged leaf area (r=0.19). Breeding lines and parents were separated into four groups of ozone sensitivity using a k-means cluster analysis of the damaged leaf area estimates. The registered white bean cultivar Seafarer was placed into the most sensitive group, while Kentwood was placed in an intermediate group. Ex Rico 23 ranked in the least sensitive group. Twenty-two breeding lines were less sensitive than their white bean parent. Six were more sensitive, and seven showed no difference from their white bean parents. Improvement was most noticeable for breeding lines derived from the early white bean cultivars Seafarer and Kentwood. Five breeding lines derived from Ex Rico 23 maintained the low sensitivity of the parent line. Cluster analysis of the standard deviation scores from the video image data placed seven breeding lines in the next higher or lower sensitivity groups set by the visual assessment of damaged leaf area. The remaining 34 lines were identically grouped. The 35 selected breeding lines along with 5 new breeding lines and 8 check varieties were planted in the yield and ozone trials at the Agriculture Canada Harrow Research Stations and the Ridgetown College of Agricultural Technology Research Station in June, 1986. Ozone damage, yield and maturity data will be collected. Approximately 10 lines will be continued in advanced trials in 1987, and ultimately, one or two lines will be entered in provincial licensing trials in 1988.

ABSTRACT FORM

Author : D.R. Hastie
Address : Chemistry Department, York University, 4700 Keele Street
Downsview, Ontario Phone (416) 736-2100 x 3846
Co-Authors : H.I. Schiff

Topic Area : Air ☒, Water ☐, Waste ☐, Analytical ☐

Environmental Economics ☐

Do you prefer presenting: A paper ☒, a poster session ☐

Title: Nickel Carbonyl Ambient Monitor

Abstract:

The Ministry had a requirement for an ambient Nickel Carbonyl monitor capable of making measurements down to the Provincial limits.

The only commercially available Nickel Carbonyl monitor was not sufficiently sensitive to fulfill the Ministry's needs. Furthermore the manufacturer was not interested in upgrading their instrument in light of the expected market.

We took a commercial NO/NOx chemiluminescent analyser and modified it to measure Nickel Carbonyl. To measure $Ni(CO)_4$ rather than NO major changes were made to the plumbing of the instrument. An additional input to allow the addition of carbon monoxide to the air stream and a permeation based air dryer was added to the inlet of the instrument to remove problems encountered with water vapour. The filter in front of the photomultiplier was changed to give maximum sensitivity towards $Ni(CO)_4$ while discriminating against $Fe(CO)_5$ and NO. The reaction vessel was increased in size to improve sensitivity. A calibration protocol was developed to allow in-situ calibrations of $Ni(CO)_4$.

The instrument has shown a linear response to $Ni(CO)_4$ over an order of magnitude range of $Ni(CO)_4$ concentrations and has a detection limit of 10 ppt.

Notes: The original photomultiplier provided with this instrument catastrophically degraded during the testing of the instrument. It has been replaced with a Hamamatsu tube. This tube does not respond in the red so does not need to be cooled, thus the fuse on the cooler circuit has been removed. It is normal for this tube to have a high but stable dark current.

ABSTRACT FORM

Author : Philip Harvey
Address : Dept. of Physics, Queen's University, Kingston, Ontario
Phone (613) 545-2673
Co-Authors : X-P.Ma., J.D. MacArthur and G.R. Palmer

Topic Area : Air ☒, Water ☐, Waste ☐, Analytical ☐
Environmental Economics ☐

Do you prefer presenting: A paper ☒, a poster session ☐

Title: Elemental Composition of Air Particulates Inside and Outside a Building

Abstract:

Air particulates have been collected simultaneously outside and in several rooms inside a school in Kingston, Ontario for two week periods, one during the heating season and the other in the late spring. The time sequence of the deposition was obtained as a streak on nucleopore filters which moved past a 2mm x 4mm nozzle at 1 mm/hr. The elemental composition of the deposit was determined with particle induced x-ray emission, a non-destructive technique which is capable of measuring minute quantities (0.5 ng) of all elements with atomic number greater than 12. The elements A1, Si, S, C1, K, Ca, Ti, Mn, Fe, Cu, Zn, Br and Pb were detected. Several factors, human motion, outside air load and human activity, determine the concentration of the elements inside the various rooms of the school. Models for the dependence of the concentrations on these factors have been developed. Through principal component factor analysis, several sources, such as soil, automobile emission and combustion were identified as contributors to the air particulates in all locations while specific sources, such as aerosols due to human activities, were found in some rooms.

ABSTRACT FORM

Author : L.C. Dickson
Address : University of Waterloo, Dept. of Chemistry, Waterloo
Ontario, N2L 3G1 Phone (519) 885-1211 Ext. 3423
Co-Authors : F.W. Karasek

Topic Area : Air ☒, Water ☐, Waste ☐, Analytical ☐

Environmental Economics ☐

Do you prefer presenting: A paper ☒, a poster session ☐

Title: Study of the Thermal Reactions of Polychlorinated Dibenzo-p-Dioxins on Flyash Particles under Incinerator Conditions.

Abstract:

Very little is known about the formation process mechanisms of chlorinated dibenzo-p-dioxins in municipal incinerators. The most acceptable mechanism is that they result from catalytic reactions on the surface of flyash particles in the incineration process. Some organic compounds and specifically chlorinated dioxins are known to undergo gas-solid reactions on flyash and have been shown to chemisorb onto the surface of flyash particles.

To investigate the possibility of gas-solid reactions producing chlorinated dioxins from precursor compounds, we constructed a simple flowtube apparatus consisting of a compressed gas supply, rotameter, a heated reaction zone containing exhaustively extracted clean flyash, a cooled impinger and a florisil guard trap. ^{13}C-labelled or unlabelled chlorinated phenols in solution were deposited on glass beads at room temperature. These beads were placed in the flowtube just upstream of the flyash. The one hour experiments were done at 300°C under a 10 mL/min. nitrogen flow.

Chlorinated dioxins with ^{13}C were recovered from the flyash and from the impinger rinse after passsing ^{13}C-labelled pentachlorophenol through the flyash from a refractory-wall incinerator located in Toronto. A similar experiment using flyash from an energy recovery municipal incinerator in Japan yielded much lower amounts of chlorinated dioxines. Only minor amounts of octachlorodioxin were produced when using a bed of ground firebrick and an empty flowtube, indicating the presence of the catalytic flyash is necessary to form the full range of dioxin congeners.

Experiments using 2,4,5-trichlorophenol and 3,4,5-trichlorophenol yielded chlorinated dioxin isomer distributions very different from each other and from that arising from pentachlorophenol. The fact a distribution of isomers is observed, rather than a single product from the condensation of two tri-chlorinated phenols, indicates that both chlorination and dechlorination reactions are occurring on the flyash surface. The production of chlorinated dioxins from 3,4,6-trichlorophenol is interesting since this compound does not possess a chlorine ortho to the hydroxyl group, which is necessary for condensation and ring closure to form dioxins.

Further experiments are underway to find correlations between the physical and chemical properties of these flyashes and their activity with respect to the production of dioxins.

ABSTRACT FORM

Author : John H. Kosch
Address : Amko Systems, Inc., 57 Patrice Crescent,
Thornhill, Ontario Phone (416) 731-0927
Co-Authors :

Topic Area : Air ☒, Water ☐, Waste ☐, Analytical ☐

Environmental Economics ☐

Do you prefer presenting: A paper ☒, a poster session ☐

Title: Continuous Emission Monitoring for Total Hydrocarbons at Sewage Sludge Incinerators.

Abstract:

Total hydrocarbon (THC) analyzers for use in stack monitoring are based on the flame ionization detector (FID).

A program was recognized in the operation of THC analyzers at sludge incinerators; frequently, the FID remains operational for only a few hours before failing and forcing system shut-down. To correct this situation, Amko Systems Inc., in consultation with the Air Resources Branch, undertook to research this problem.

Our monitoring package consisted of a heated dilution system (ADS), developed by us, that was connected to one ratfisch FID total huydrocarbon analyzer. Signal was connected to the strip chart recorder.

The ADS was designed to 1) coarse and fine filter the incoming sample, 2) proportion dilution air, with use of a differential pressure regulator, into the sample capillary and 3) progressively elevate the sample temperature as it is drawn towards the analyzer. The sample is, in this process, fed through the filters at approximately 130°C, into the capillary at 140°C and into the FID at 160°C. The problem of the condensation of high boiler organics is thus addressed.

The dilution ratio chosen for this facility was a moderate 1:1.

Results

The Dilution system functioned for a continuous time of 559 hours before requiring maintenance of a 15 minute filter change.

During the entire 32-day test period, the dilution ratio did not vary by more than ±2.5% of the initial value.

Zero drift was, for this purpose, negligible.

The result of this project indicates our heated dilution system to be a viable approach to achieving acceptable up-times for hydrocarbon analyzers in sewage sludge incinerators. (The system on location for the previous seven years did never operate for more than three days continuously).

ABSTRACT FORM

Author : E.A. McBean
Address : Dept. of Civil Engineering, University of Waterloo
Ontario, N2L 3GL Phone (519) 885-1211, Ext. 3349
Co-Authors : J. Byrne, J. Donald and G.J. Farquhar

Topic Area : Air ☒, Water ☐, Waste ☐, Analytical ☐
Environmental Economics ☐

Do you prefer presenting: A paper ☒, a poster session ☐

Title: Study of the Spatial Distribution of the Impact of Sudbury Smelting Emissions.

Abstract:

The two mining and smelting operations near Sudbury are the source of greater than half of the total SO_2 emissions in Ontario (Tang et al, 1984). These releases are examined to improve the understanding of the resulting areal deposition patterns. The intent of this focus is three fold:

(i) to develop contouring procedures which will allow generalization of point-specific measured information and to indicate percentages of regions which would be impacted by various levels of remedial control-technologies;

(ii) to better understand the long-term deposition levels, reflecting meteorologic variability on annual and seasonal levels; and,

(iii) to compare with monitoring station records to observe whether additional and/or fewer monitoring stations may be appropriate.

ABSTRACT FORM

Author : Geoff Ogram
Address : Ontario Hydro, 800 Kipling Avenue, Etobicoke, Ontario
Phone (416) 231-4111/ext. 6536
Co-Authors : H. Sahota and P.K. Misra

Topic Area : Air |x|, Water | |, Waste | |, Analytical | |

Environmental Economics | |

Do you prefer presenting: A paper |x|, a poster session | |

Title: Characterization of Building Wake Effects at Darlington Nuclear Generating Station using Sulfur Hexafluoride (SF6) as a Tracer.

Abstract:

A field experiment was conducted at Darlington nuclear generating station to investigate the effects of the structure on the effluents released from the top of the vacuum building and the power station building. Sulfur hexafluoride (SF6) was released for three to four hours, and sampling was carried out on fixed arcs and with a real time monitor mounted in a mobile van. Simultaneous meteorological data was collected with a doppler acoustic sounder, and four instrumented meteorological towers located on the site.

Under moderate winds, mixing in the building wake was quite evident. The plume was observed to be well mixed and well defined. Under light winds the plume was not discernible and under strong winds, large fluctuations in (SF6) concentration were observed at a fixed location. Analysis of the data is under way to quantify the impact of the vacuum building and the generating station building, on the dispersion of effluents released from top of these structures.

SESSION B

WATER QUALITY RESEARCH

ABSTRACT FORM

Author : Dora R. May Passino
Address : U.S. Fish and Wildlife Service, Ann Arbor,
Michigan, 48105, U.S.A. Phone (313) 994-3331
Co-Authors :

Topic Area : Air ☐, Water ☒, Waste ☐, Analytical ☐
Environmental Economics ☐

Do you prefer presenting: A paper ☒, a poster session ☐

Title: Predictive Models in Hazard Assessment of Great Lakes Contaminants for Fish.

Abstract:

A hazard assessment scheme was developed and applied to predict potential harm to aquatic biota of nearly 500 organic compounds detected by GC/MS in Great Lakes fish. The frequency of occurrence and estimated concentrations of compounds found in lake trout (*Salvelinus namaycush*) and walleyes (*Stizostedion v. vitreum*) were compared with available manufacturing and discharge information. Bioconcentration potential of the compounds was estimated from available data or from quantitative structure-activity relationship (QSAR) calculations. We also measured the acute toxicity to *Daphnia pulex* (48-h EC50's) of 35 representative compounds and compared the results with acute toxicity values generated by QSAR. The QSAR-derived toxicities for several chemicals underestimated the actual acute toxicity by one or more orders of magnitude. A multiple regression of log EC50 on log water solubility and molecular volume is a useful predictive model. Additional models providing insight into toxicity utilize solvatochromatic parameters that measure dipolarity/polarizability, hydrogen bond acceptor basicity, and hydrogen bond donor acidity of the solute (toxicant).

ABSTRACT FORM

Author : Henryk Melcer
Address : Environment Canada, Wastewater Technology Centre,
Burlington, Ontario Phone ( ) 336-4740
Co-Authors :

Topic Area : Air ☐, Water ☒, Waste ☐, Analytical ☐

Environmental Economics ☐

Do you prefer presenting: A paper ☒, a poster session ☐

Title: The Control of Toxic Trace Contaminants in Municipal Wastewater Treatment Plants.

Abstract:

The removal of toxic trace contaminants in activated sludge treatment plants occurs by volatilization, adsorption and biological degredation. Data will be shown to demonstrate these phenomena for activated sludge systems treating municipal wastewaters. It has been established that many trace contaminants can be removed successfully if biological treatment plants are operated at high SRTs. A surrogate parameter that may be used to ensure plants are operating at high SRTs is that of nitrification. Data will be presented to substantiate this supposition. The variability of trace contaminants in municipal wastewater is not established. Data from an ongoing study that addresses the measurement and control of varying concentrations of trace contaminants will be presented.

ABSTRACT FORM

Author : J.N. Hilton
Address : MacLaren Plansearch Inc., 33 Yonge Street
Toronto, M5E 1E7 Phone (416) 365-7275
Co-Authors : R.M. Machacek

Topic Area : Air ☐, Water ☒, Waste ☐, Analytical ☐

Environmental Economics ☐

Do you prefer presenting: A paper ☒, a poster session ☐

Title: Trace Organic Contaminant Removal From Drinking Water

Abstract:

As public concern for the quality of drinking water in Ontario continues to grow, considerable research has been undertaken to re-examine conventional treatment methodologies as well as alternate processes for the removal of trace levels of organic chemicals, including adsorption by granular activated carbon (GAC).

This project has been undertaken to determine the following:

- the effectiveness of optimized conventional drinking water treatment for the removal of trace organic contaminants;
- the effectiveness of activated carbon adsorption removals of trace organic contaminants when used in the add-on contactor mode.
- process operational parameters for the optimized operation of full scale water treatment plants and GAC adsorbers used in the add-on mode for organics removal;
- process operational parameters for the optimized operation of full scale water treatment plants and GAC adsorbers used in the add-on mode for organics removal.

Jar testing and pilot plant operations are being conducted on site at the Niagara Falls Water Treatment Plant, using the Niagara River as the raw water source.

In this paper the results of the jar testing program to select chemicals to optimize the conventional treatment process for organics removal are discussed. Further the conventional treatment process evaluation methodology and results are discussed based on the operation of the pilot plant.

ABSTRACT FORM

Author : R.C. Starr
Address : Dept. of Earth Sciences, University of Waterloo
Ontario, N2L 3G1 Phone (519) 885-1211 x 3159
Co-Authors : R.W. Gillham

Topic Area : Air ☐, Water ☒, Waste ☐, Analytical ☐

Environmental Economics ☐

Do you prefer presenting: A paper ☒, a poster session ☐

Title: The Role of Organic Carbon in Controlling the Occurrence of Denitrification in Groundwater.

Abstract:

The role of organic carbon in controlling the occurrence of denitrification in two sandy, unconfined aquifers beneath agricultural land in Southern Ontario was investigated. Initial field monitoring showed denitrification to be an active process in an aquifer with a watertable close to ground surface, but to be relatively unimportant in a second aquifer with a much deeper watertable. It was postulated that the occurrence of denitrification was controlled by the availability of labile organic carbon. Profiles from ground surface to below the watertable of solid and dissolved organic carbon, and the ability of subsurface materials to support denitrification in the laboratory were generated. The results indicate that the ability of subsurface materials to support denitrification depends on the size of the organic carbon pool, and that denitification is carbon-limited at depth.

The rate of denitrification was measured in-situ in both aquifers, with and without the addition of organic carbon. Denitrification occurred without but was enhanced by, the addition of organic carbon at the denitrifying site. This indicates that although sufficient carbon was present to support denitrification, the rate was limited by carbon availability. At the non-denitrifying site denitrification did not occur unless organic carbon was added. This demonstrates that the non-occurrence of denitrification in this aquifer is due to the lack of a sufficient source of organic carbon for denitrifying bacteria. Denitrification was not limited at either site by the absence of denitrifying bacteria.

ABSTRACT FORM

Author : James McD. Robertson
Address : Epidemiology and Biostatistics Kresge Building
London, Ontario Phone (519) 661-2161
Co-Authors : Harvey J. Chan, I.M. Fyfe

Topic Area : Air ☐, Water ☒, Waste ☐, Analytical ☐

Environmental Economics ☐

Do you prefer presenting: A paper ☒, a poster session ☐

Title: Reproductive Outcomes in Southwestern Ontario, 1980 to 1985

Abstract:

This epidemiologic study, supported jointly by the Ministry of the Environment and the Ministry of Health, was designed to determine if drinking water from the St. Clair River was associated with increased risks of adverse outcomes of pregnancy and mortality in the first year of life. The outcomes of interest include: spontaneous abortion, stillbirth, low birth weight, selected congenital anomalies and perinatal, neonatal and infant mortality. First, the frequencies of these outcomes in the populations of Kent and Lambton Counties will be compared with those of the Ontario Southwest Region and the Province as a whole to determine if any excesses occurred. Second, the approximately 400 mothers in Kent and Lambton Counties who experienced, or whose children experienced, abnormal outcomes and a like number of individually-matched control mothers will be interviewed to assess their sources of drinking water during the index pregnancy and to document the frequencies of several other variables known to be associated with the outcomes of interest. Third, this study will examine the relationship between the occurrence of adverse outcomes and specific chemical spills by comparing the outcomes of pregnancy in a cohort of exposed women with those of a matched cohort of unexposed women.

ABSTRACT FORM

Author : Scott Abernethy
Address : University of Toronto
Toronto, Ont. M5S 1A4 Phone (416) 978-4019
Co-Authors : Donald Mackay

Topic Area : Air ☐, Water ☒, Waste ☐, Analytical ☐

Environmental Economics ☐

Do you prefer presenting: A paper ☒, a poster session ☐

Title: Organic Contaminant Structure-Property-Toxicity Relationships for Aquatic Organisms.

Abstract:

Two intercalibrated toxicity test systems with *Daphnia* and *Artemia* have provided consistent acute lethality data for hydrocarbons and chlorinated hydrocarbons in aqueous solution. Significant quantitative structure-activity relationships (QSARs) have been and continue to be established with these tests for several classes of pollutants which are of concern to the MOE. These QSARs can provide information which is of assistance in the formulation of Provincial Water Quality Objectives. These empirically-derived QSARs are used to validate and refine proposed toxicity models or simple "rules of thumb", which in turn provide estimates of toxicity based on properties of the chemical, for situations in which experimental toxicity data are unavailable. The importance of molar volume for estimating toxicity has recently been assessed (by re-analyzing our data and that of other workers) and will be discussed in terms of these toxicity models.

Since pollutants most often occur at sub-lethal levels and in mixtures, QSARs are being developed to treat such situations. One aspect is the development of a 7d life cycle test with *Ceriodaphnia* to provide chronic toxicity data for single compounds and simple mixtures. This work will be described and discussed in a QSAR framework.

ABSTRACT FORM

Author : D.M. Nicholls
Address : Dept. of Biology, York University, 4700 Keele Street,
North York, M3J 1P3 Phone (416) 736-5273
Co-Authors : R. Angelow, T. Teichert-Kuliszewska and G. Girgin
(Dept. Chem. Tech. Seneca College)
Topic Area : Air ☐, Water ☒, Waste ☐, Analytical ☐

Environmental Economics ☐

Do you prefer presenting: A paper ☒, a poster session ☐

Title: Effect of Lead, Cadmium and Mercury on the Tissue of Young Fish and Rats: Development of a Bioindicator.

Abstract:

Exposure of fish to heavy metals in the laboratory, in static and flow bioassays, and in Ontario lakes, has been studied by measuring key enzymes involved in growth. There has been a scarcity of information on disturbances of the function of protein synthesis, energy-producing glycolytic enzymes and membrane interfacial enzymes in fish following low and high levels of toxic metal in the water. Thus we are correlating these activities with the metal levels in the animal in order to develop a more sensitive bioindicator test.

Fish exposed to Hg (30 ug/l) for six weeks exhibited statistically significant decreases in the enzymes of protein synthesis both in the liver, and also in the muscle, thus indicating an important reduction in the capability for growth. Fish from impacted lakes showed similar results.

Shorter exposure to higher Hg levels resulted in similar disturbances of protein synthesis. Low levels of Hg (e.g. 0.1 ug/l) trigger mRNA in fish liver for such activities as metallothionein gene expression.

Four glycolytic enzymes were measured in fish livers and muscle after exposure to Hg (30ug/l) for 3 or 6 weeks, and in fish from impacted lakes. Lactic dehydrogenase (LD) activity and glyceraldehyde-3- phosphate (GAP) dehydrogenase activity were decreased up to 50% under the most severe conditions.

Three "marker" enzymes of the membrane interface between the cell and its extracellular environment were also studied because: (1) heavy metals such as Hg are believed to disrupt the integrity of the membrane, and (2) these enzymes might be useful for easily conducted field assays. Contrary to what was expected, only modest effects of heavy metal exposure were observed in one of the three enzymes: &-glutamyl transpeptidase. This enzyme plays an important role in the transport of amino acids in tissues.

Exposure of fish to combinations of Cd (0.25ug/l) and Pb (25ug/l) with Hg (0.25 ug/l) did not exhibit a synergistic effect upon the protein synthesis and glycolytic enzymes, thus confirming separate experiments on mammals.

The results of this work show that we can use certain enzymes as sensitive indicators of Hg toxicity.

ABSTRACT FORM

Author : K.R. Munkittrick
Address : Dept. Biology, University of Waterloo, Waterloo
Ontario, N2L 3G1 Phone (519) 885-1211 X 2531
Co-Authors : D.G. Dixon

Topic Area : Air ☐, Water ☒, Waste ☐, Analytical ☐
Environmental Economics ☐

Do you prefer presenting: A paper ☒, a poster session ☐

Title: In Situ Assessment of Mixed Copper and Zinc Impacts on White Sucker (*Catastomus commersoni*) Populations in Several Northern Ontario Lakes: An Evaluation of the Environmental Health Approach to Validating Water Quality Criteria.

Abstract:

Several lakes in the Manitouwadge district of Northern Ontario exhibit elevated levels of copper (11-13 ug/l) and zinc (220-236 ug/l) associated with mining activities. Since reproductive capacity may potentially represent the most toxicant-sensitive facet of a fish's life history, white sucker populations in the Manitouwadge district were examined for evidence of reproductive impairment associated with their chronic exposure to elevated metals. Fish from metal contaminated lakes showed decreases in length, weight and growth relative to the control site. They also exhibited an increased heptosomatic index and an increased incidence of failure to spawn. Although there were no demonstrated differences in fertilization rate in the laboratory, or in situ, this study suggests that there are significant impacts of chronic exposure to waterborne metals which are not evident from a cursory examination of reproductive potential. The increased relative fecundity, decreased egg size, increased milt volume, normal fertilization rate and natural fungicidal properties of waterborne copper appear to result in the presence of enormous numbers of sucker eggs on the spawning beds of metal contaminated sites. Eggs collected from fish at contaminated sites hatched into larvaelarvae which exhibited significantly decreased length and weight relative to control sits, as well as increased developmental rate, poorer conversion to exogenous feeding and a marked decrease in survival time in the absence of food. It is unclear at this time whether a further decrease in egg size evident after in situ fertilization would result in a reduced recruitment to the lake population, despite an apparent increase in the numbers of eggs released. Although eggs hatched in the laboratory were never exposed to metals, larvae coming from contaminated sites were consistently more resistant to toxic levels of copper than were control larvae, except for a brief period during transition to exogenous feedings. Effects of both age and food availability were noted on both the tolerance and resistance of the larvae to copper exposure.

ABSTRACT FORM

Author : Brian Clark
Address : Depts. of Chem. Eng. & Appl. Chem. and Civil Engineering
Univ. of Toronto Phone (416) 978-4019
Co-Authors : Sandra Salenieks, J. Glynn Henry, Donald Mackay

Topic Area : Air ☐, Water ☒, Waste ☐, Analytical ☐

Environmental Economics ☐

Do you prefer presenting: A paper ☒, a poster session ☐

Title: The Fate of Toxic Organic Chemicals in Sewage Treatment Plants.

Abstract:

A predictive model describing the fate of organic chemicals in a water pollution control plant has been developed, based on the "fugacity" modelling system. By estimating a prevailing fugacity in each of the primary, aeration, and secondary settling tanks, chemical concentrations in the water, air, and sludge can be calculated. Thus fluxes can be estimated and a mass balance assembled.

Comparison of the fugacity model with the predictive fate models developed by Blackburn, et al. and Roberts, et al. and other workers show good agreement.

The fugacity model was also subjected to tests of validity by the following methods:

1) conducting laboratory-scale experiments for chemical stripping, stripping-sorption and stripping-sorption and biodegradation and comparing experimental results with the predicted values.

2) comparing the fugacity model predictions with data obtained form the literature, and from full-scale water pollution control plants.

In all cases, it was observed that the model predicted the fate of organic chemicals with fair accuracy based on reasonable estimates of biodegradation rate constants. It is concluded that the model can be used to give estimates of the fate of organic contaminants in treatment plants.

ABSTRACT FORM

Author : N.K. Kaushik
Address : University of Guelph, Guelph, Ontario, N1G 2W1
Phone (519) 824-4120 ext. 2147
Co-Authors : G.L. Stephenson

Topic Area : Air ☐, Water ☒, Waste ☐, Analytical ☐
Environmental Economics ☐

Do you prefer presenting: A paper ☒, a poster session ☐

Title: Toxicity of Pentachlorophenol to Zooplankton

Abstract:

A static with renewal chronic toxicity test was used to evaluate the impact of sublethal concentrations of pure (99.9%) pentachlorophenol (PCP) and a technical (82.0%) formulation of pentachlorophenol on the life history criteria of Daphnia magna. The daphnids used in the experiment were produced by a cohort of adults exposed to the test conditions in an environmental chamber (temperature - 20.0 ± 1°C; photoperiod - 16 light:8 dark h). The experimental design included three concentrations of pure and four of technical PCP. There were 20 daphnids in each treatment, one daphnid per beaker with 80mL of test solution in each beaker. Test solutions were made form the stock solutions of PCP (1,000 mg/L) by dilution with aerated well water and an acetone equivalent of the maximum PCP concentration served as controls. Test solutions were renewed every second day at which time the organisms were fed 2.5 mg green algae/L. The experiment was conducted over the entire lifespan of each daphnid (max. 164 d) and the impact of PCP on longevity, time to appearance of the primiparous instar, time to release of first brood, number of young produced per daphnid, number of moults and production of ephippia was evaluated. The results of this experiment will be summarized and presented in a poster presentation pending analysis of these data.

ABSTRACT FORM

Author : Al Melkic
Address : Integrated Exploratins, P.O. Box 1385
Guelph, N1H 6N8 Phone (519) 822-2608
Co-Authors : Edward Creese, Donald Lewis

Topic Area : Air ☐, Water ☒, Waste ☐, Analytical ☐

Environmental Economics ☐

Do you prefer presenting: A paper ☒, a poster session ☐

Title: Development of a Standard Clam Biomonitoring Methodology for the Detection of Trace Contaminants within Water of the Ontario Great Lakes Region.

Abstract:

Clams have been used for several years by the Ontario Ministry of the Environment for the detection of trace contaminants of several types. The method has proved successful in locating contaminant plumes and cross-boundary contamination in rivers. The method has two advantages over strictly chemical monitoring. The first is that the results are time-integrated over the entire exposure period and the second is that it yields a direct measurement of a biological effect.

The source of clams to date has been one of the Kawartha Lakes, Balsam Lake. **Elliptio complanata** is the species that has been used until now. Part of our work has involved searching for new sources of uncontaminated clams, possibly clams of other species.

The rest of our work has been experimental in nature. There was a need to determine what effect, if any, certain factors have on the uptake of trace contaminants. Choosing Niagara-on-the-Lake as an experimental site, we have looked at the effects of different methods of transportation and deployment of clams and preservation of clam tissues on measured uptake of PCB's. Different methods of transportation included transporting clams at various temperatures in water or merely moist in air. The deployment methods that were tested involved different types of clam cages in which clams may filter river water to a greater or lesser extent. Preservation methods included storage of live clams on ice for a short period of time and immediate shucking followed by freezing on dry ice. We have also experimentally varied the temperature of the river water to see the effect of this variable on PCB uptake.

ABSTRACT FORM

Author : Merv Palmer
Address : Gore & Storie Limited, 1670 Bayview, Toronto,
Ontario Phone (416) 485-7715
Co-Authors :

Topic Area : Air ☐, Water ☒, Waste ☐, Analytical ☐
Environmental Economics ☐

Do you prefer presenting: A paper ☒, a poster session ☐

Title: Evaluation of Data on the Effects of Hydraulic Characteristics and Effluent Chlorination on the Incidence of Micro-Organisms of Public Health Significance in Receiving Waters.

Abstract:

The bacteriological impact of treated municipal effluent discharges to natural water bodies was analyzed. The studies used data gathered for the Ontario Ministry of the Environment by BEAK Consultants Limited during 1979-80 at the following sites:

- Thames River at Ingersoll
- Grand River at Grand Valley
- Otonabee River at Peterborough
- Lake Ontario at Port Hope

The review of raw data and the analyses focused on three objectives:
(1) selection of mathematical models and evaluation of their applicability;
(2) determination of travel times in receiving waters at which the total and fecal coliform (TC and FC) densities are reduced to 1000/100 mL, respectively, for both chlorination and nonchlorination periods; and
(3) establishing probabilistic distributions of pathogenic bacterial densities when (a) TC density range is 100 to 1000/100 mL or FC density range is 10 to 100/100 mL, and (b) TC density range is 1000 to 10,000/100 mL or FC density range is 100 to 1000/100 mL.

The state-of-the-art models suitable for the studies were reviewed in conjunction with the available data. The plug flow model was selected to be suitable for each river site. The lake site had large fluctuations and/or insufficient information, and hence, the data were not analysed. Plug flow model predictions for individual sampling days at each river site were in reasonable agreement with measured values in most cases within a factor of one-half log cycle.

The travel times at which the TC and FC densities reach 1000/100 mL and 100/100 mL, were smaller for the disinfected effluent discharges compared to the nondisinfected discharges and were affected by receiving water densified of TC and FC.

The correlations between the pathogenic and indicator bacteria were very poor for the Grand and Thames River sites. The Otonabee River data showed correlations between: (a) Klebsiella and TC; (b) P. aeruginosa and FC; and (c) Klebsiella and FC when the data are partitioned to eliminate low values biases and to consider the sensitivity of the bacterial density determination.

ABSTRACT FORM

Author : Joan M. Herskowitz
Address : Water Resources Branch, MOF, 1 St. Clair Ave. West
Toronto, Ontario Phone (416) 965-1655
Co-Authors : Steve A. Black and Werner Lewandowski

Topic Area : Air ☐, Water ☒, Waste ☐, Analytical ☐
Environmental Economics ☐

Do you prefer presenting: A paper ☒, a poster session ☐

Title: Listowel Artifical Marsh Treatment Project

Abstract:

Five separate cattail (Typha spp.) marsh treatment systems, occupying a total area of 8670 m^{2}, were operated for four years (1980-1984). Several different marsh designs and two pre-treatment types, namely, complete-mix aeration cell effluent (average BOD5=60 mg L-^{1}) and lagoon effluent (average BOD5=20 mg L-^{1}), diverted from the existing Town of Listowel sewage works, were tested. The method of pre-treatment was shown to influence marsh operation and the quality of the final marsh effluent. Channelized marshes yielded the highest treatment efficiencies as this configuration provided greater control over flow distribution and wastewater retention time. Removal efficiencies declined when the hydraulic detention time, regulated by seasonal adjustments in water depth, deviated from the range of 7-14 days.

Marsh effluent quality achieved in the experimental systems was at levels between conventional secondary and tertiary treatment. The four year annual average effluent quality in the channelized marshes in terms of BOD5, SS, TP and TKN was 7.6, 9.2, 0.5 and 6.2 mg L-^{1}, respectively, in the system receiving lagoon effluent (System 3) and 9.6, 8.0, 0.6 and 8.7 mg L-^{1}, respectively, in the system receiving aeration cell effluent (System 4).

Large BOD reductions were maintained throughout the year, including winter months when average wastewater temperatures were less than 2°C. Elevated ammonia, hydrogen sulphide and phenol levels in the marsh effluent in summer and at the end of the winter season were attributed to anaerobic conditions, whereas low temperatures appeared to be the major factor in decreased ammonia removal in the winter months. The observed decline in annual phosphorous retention suggests progressive saturation of the phosphorus adsoption capacity of the sediment. Large reductions in fecal bacteria were achieved in the marshes although in some months levels exceeded Ministry objectives for disinfected effluent. Increased removal efficiencies, resulting from the implementation of pilot study recommendations, are expected in the full-scale marsh treatment facility currently in operation at Port Perry, Ontario.

ABSTRACT FORM

Author : J.D. Boadway
Address : Department of Civil Engineering
Queen's University Phone (613) 545-2139
Co-Authors : Kingston, Ontario

Topic Area : Air ☐, Water ☒, Waste ☐, Analytical ☐

Environmental Economics ☐

Do you prefer presenting: A paper ☒, a poster session ☐

Title: A Low Pressure Hydrocyclone for Use in Sewage Treatment

Abstract:

The objective of this project is to explore the possible use, in sewage treatment, of a new form of hydrocyclone, which can be operated at very low pressure differentials due to recovery of kinetic energy. While the major emphasis in the project is on efficient removal of fine grit there is also the possibility of using such a system for removal of faster settling organics thus replacing some primary clarification.

Rather than using designs of hydrocyclone similar to those used in other industries, it was decided that a special design should be developed to fit the special needs of the sanitary treatment process. The unit should have a large enough capacity to avoid installations with large banks of units, should have large enough clearances to avoid blockages, should be able to remove over 90% of 200 mesh sand particles and should be short enough to fit into a building with modest headroom.

The final design of hydrocyclone made to fit these needs with estimated hydraulic capacity and separating performance based on tests of similar smaller units is as shown below:

Dimensions	
Barrel diameter	25 inches or 63 1/2 cms
Piping size	6 inches or 15 1/4 cms
Length	7 feet or 2 1/8 meters

Performance at 3 meters pressure differential
Flow 445 USgpm or 28 litres/second
Grit size removable at 50% efficiency 35 microns
Overflow rate 15 USgpm/sq.ft. or
(Clarifier Equivalent) 10.5 litres/sq.m. second

The predicted overflow rate is roughly 1/10 that used for design of grit channels and 25 times that of most primary clarifiers.

The research plan involves preliminary testing on controlled media at the University to evaluate flow and solids removal prior to installation in the field. The arrangement for this laboratory testing is almost completed and the results will be presented. A discussion of the nature of hydrocyclone and how specially designed units might be used in treatment of municipal and industrial effluents will also be included in the presentation.

ABSTRACT FORM

Author : B.H. Hindley
Address : MTRCA 5 Shoreham Drive, North York, Ontario
M3N 1S4 Phone (416) 661-6600 X-246
Co-Authors : R.P. Hubbard

Topic Area : Air ☐, Water ☒, Waste ☐, Analytical ☐

Environmental Economics ☐

Do you prefer presenting: A paper ☒, a poster session ☐

Title: The Effects of Rural and Suburban Development on Surface Water Quality in Five Selected Subwatersheds on the Upper Humber River.

Abstract:

Previous research on the Upper Humber River indicated a combination of diffuse and point-source inputs were responsible for the observed widespread water quality degradation. The present study was conducted to assess in greater detail the relative pollutant contributions from five of the most predominant land use types within the watershed: suburban construction, agricultural row crops, livestock access, streambank erosion and undisturbed forest. The five study subwatersheds, ranging in size from 2.6 to 21.9ha were all located in the northwestern portion of the Humber River watershed. Surface water samples, under dry, wet and spring melt conditions, were collected at stations immediately upstream and downstream of each land use area, eliminating as much as possible any extraneous inputs. Bed sediment and soil samples were also collected on occasion and bed load samplers and off-stream sediment traps installed. Preliminary results indicate severe microbiological pollution occurring through the livestock subwatershed under all weather conditions. With one exception, fecal coliform densities ranged from approximately 200 to 500,000 counts/100ml during dry weather and FC concentrations in downstream bed sediments exceeded 4500 counts/gm sediment. Suprisingly high FC concentrations were also noted within the heavily forested "Control" subwatershed; possible sources are suggested. Concentrations of chemical parameters generally appeared low within all subwatersheds under dry weather conditions. Spring melt and wet weather data are currently being analysed. On the basis of hydrologic and precipitation data, annual parameter loadings are estimated for each study subwatershed and the results generalized to the entire Upper Humber River basin.

ABSTRACT FORM

Author : Patricia L. Seyfried
Address : Dept. of Microbiology, University of Toronto
Toronto, Ontario Phone (416) 978-3732
Co-Authors : Elizabeth M. Harris

Topic Area : Air ☐, Water ☒, Waste ☐, Analytical ☐

Environmental Economics ☐

Do you prefer presenting: A paper ☒, a poster session ☐

Title: Humber River/Black Creek: Detailed Bacteriological Water Quality Study Examining the Impact of Sediment and Survival Times.

Abstract:

Studies to assess the effect of sediment resuspension upon bacterial loading of the water column were carried out at six sites along the upper and lower Humber River and Black Creek. Bacterial contribution from sediment was measured during dry weather (before and after mechanical agitation of the sediment); wet weather; and intermediate periods within two days after a rainfall. The results showed that during dry weather, at locations with consistently high point source bacterial loadings, samples taken from the water column after mechanical sediment agitation exhibited higher fecal coliform and *Escherichia coli* counts than samples taken before agitation. During wet weather, bacterial densities were usually observed to be higher than those induced by dry weather sediment agitation. This suggests that localized sediment resuspension is only one of a number of sources of bacterial pollution during storm events.

The survival rates of water quality indicator bacteria were also monitored to determine their response to the Humber River environment. Bacterial survival was found to be somewhat influenced by site-specific factors such as temperature and nutrient input For example, *E. coli* exhibited a 80 to 98% die-off rate within 24 hours at sites impacted upon by sewers, while a greater than 99% die-off rate was noted as sites not receiving nutrient enriched effluents. *Streptococcus faecalis* exhibited die-off rates similar to *E. coli* at most of the sites, whereas *S. faecium* survived somewhat longer. All three indicators survived better when the water temperature was lower than 10°C. *Streptococcus bovis* was found to exhibit rapid die-off in surface waters, i.e. greater than 99% in 24 hours.

ABSTRACT FORM

Author : Paul McKee
Address : Beak Consultants Limited - 6870 Goreway Drive
Mississauga, Ontario   Phone (416) 671-2600
Co-Authors : Karen Clarke-Whistler and Geza N. Gaspardy

Topic Area : Air ☐, Water ☒, Waste ☐, Analytical ☐

Environmental Economics ☐

Do you prefer presenting: A paper ☒, a poster session ☐

Title: Feasibility of Plant Harvesting in Water Quality Amerlioration and Phosphorus Management in Shallow Impoundment.

Abstract:

In a survey of southern Ontario reservoirs, eutrophication, as indicated by aquatic weed proliferation and/or algal blooms, was reported as a major management problem in over 80% of the impoundments. Aquatic plant harvesting may be useful in nutrient management in the reservoirs. In shallow impoundments where macrophyte biomass is high relative to the total volume of water, long-term harvesting, combined with control of nutrient sources, may effectively reduce loadings to downstream waters.

The Orangeville Reservoir, located at the headwaters of the Credit River, is highly eutrophic and contains heavy growth of aquatic macrophytes (Myriophylum spp.). The Credit Valley Conservation Authority wishes to maintain or improve water quality and to improve the recreational potential of the reservoir. To this end, a mechanical plant harvesting program was initiated in 1984. This study evaluates the harvesting program and its potential for water quality improvement in Orangeville Reservoir.

Based on an estimated input-output budget for phosphorus and nitrogen in a preliminary, the reservoir was found to act as a nutrient sink. The major storage compartment for both nitrogen and phosphorus was the highly organic sediments. Net phosphorus retention by aquatic vegetation was small; therefore, it is unlikely that plant harvesting will reduce phosphorus concentrations in the water. This was attributed to most of the phosphorus used by plants being obtained from the sediments. There was no indication of phosphorus release during winter die-off, suggesting that phosphorus tied up in the plants is returned to the sediments. On the other hand, up to 55% of total nitrogen requirements of plants appeared to be met from the water column. Thus, harvesting represents a potentially effective method of nitrogen control.

The monitoring program has been expanded and is being continued through one full year (1986) using more intensive water quality sampling and stream flow measurements to refine the nutrient budgets and to determine harvesting optimality in biomass and nutrient removal in the reservoir. The 1986 program will be complete in December 1986, and will be reported in early 1987.

ABSTRACT FORM

Author : Calum Ewing
Address : Life Sci. Div., Scarborough Campus,
University of Toronto Phone (416) 284-3218
Co-Authors : C. Nalewajko

Topic Area : Air ☐, Water ☒, Waste ☐, Analytical ☐

Environmental Economics ☐

Do you prefer presenting: A paper ☒, a poster session ☐

Title: Two Bioassays for the Rapid Determination of the Effects of Dredged Sediment Disposal on Primary Production and Phosphorus Kinetics in Open Waters.

Abstract:

The open water disposal of dredged lake sediments can have potential toxic effects on the primary production in the receiving waters. In addition, the availability of nutrients and their cycling can be greatly affected. To date studies of dredgeate toxicity have examined only the effects on photosynthesis and have used only the sediment elutriates to assess toxicity. We now present two bioassays that (1) allow the determination of toxic effects of whole sediments on primary production, as opposed to sediment elutriates or extracts, and (2) allow determination of the effects of whole sediments and elutriates on phosphorus cycling.

The effects of Lake Ontario sediments on the primary production and phosphorus kinetics of epilimnetic phytoplankton assemblages were investigated. Sediment toxicity was assessed using sediment elutriates and whole sediments. The effects of both, on primary production, were measured using the incorporation of ^{14}C, into DMSO extractable compounds, over a range of irradiances. Elutriates prepared from polluted (Niagara River Mouth) and unpolluted (Mid Lake) sediments failed to show any toxic effect at a 10% (v/v) dosage, but whole sediment depressed the maximal photosynthetic rate (Pmax) by up to 70%.

The effects of sediment disposal on phosphorus cycling were assessed using $^{32}P\text{-}PO_4$ uptake kinetics. Phosphate turnover time was found to increase in a linear fashion with elutriate dosage. This effect was much greater with the Mid Lake elutriates. The addition of whole sediment caused much greater increases in turnover time than was seen with elutriates. The addition of heat killed sediment caused increases in turnover time lower than those shown by the lutriates.

The observed effects are best explained by the high concentrations of phosphorus and toxic chemicals that are present in the sediments but not extracted during the elutriation process. The high concentration of bacteria in the sediment and its physicochemical properties of sediments may plan an important role. These bioassays can be used to rapidly assess the potential toxic effects of dredged sediments, before disposal in open water.

ABSTRACT FORM

Author : V.A. Graham
Address : Dept. of Systems Design, University of Waterloo
Waterloo, Ont. N3L 3G1 Phone (519) 885-1211, ext. 2870
Co-Authors : T.E. Unny and L. Logan

Topic Area : Air ☐, Water ☒, Waste ☐, Analytical ☐

Environmental Economics ☐

Do you prefer presenting: A paper ☒, a poster session ☐

Title: Stochastic Estimation of Ambient Water Quality in the Thames River.

Abstract:

Quantifying the variations in water quality parameters is essential to developing objective policy for the management and control of toxic contaminants in Ontario streams. In this regard, research into the probability and stochastic features of phosphorous and suspended sediment concentrations in the Thames river has been performed. Mathematical models describing these features have been developed for monthly water quality events. Investigation in the probability behaviour of these events reveal that the governing probability distribution was not fixed for all months, but would change on a monthly basis. These distributions were also observed to be strongly non-Gaussian. The probability density functions were described using a five parameter polynomial expressions. This model successfully preserved the key moments (mean, variance, skewness, and kurtosis) of the historic water data).

Stochastic models for the phosphorous and suspended sediment concentrations were developed using the ARIMA process. Since this family of processes require that the underlying distributions for monthly events be Gaussian and time-invariant, novel transformations methods were developed for mapping monthly water quality data from its parent distribution to a N(0,1) distribution, for all months. The model constructed for the transformed monthly phosphorous variable as an ARIMA [1,1,0], with an autoregressive parameter estimate $\emptyset_1$ of -0.546. Transformed suspended sediment data was adequately described using a white noise ARIMA [0,0,0] model.

The modeling methodology developed in this research provides a solid framework for modeling water quality data from various streams. These data are likely to be non-Gaussian and represented by distributions that change monthly. The devised transformation guarantees that the probability distribution of the observed series is incorporated in the model. Hence synthetic water quality events generated using these models are bound to reproduce the complex non-Gaussian time-varying probability distributions, while representing the serial relationship between consecutive monthly events. This methodology also allows stochastic models to be developed for streams with substantial missing values, without having to make any assumptions about the character of the missing values, and thus provides a rational basic for "filling-in" missing values in the large set of historic record kept by the Ministry of the Environment.

ABSTRACT FORM

Author : M.D. Palmer
Address : Gore & Storrie Limited, 1670 Bayview Avenue, Toronto,
Ontario, M4G 3C2 Phone (416) 485-7715
Co-Authors : C. Arnoldi, T.P.H. Gowda, R. Jarvis

Topic Area : Air ☐, Water ☒, Waste ☐, Analytical ☐
Environmental Economics ☐

Do you prefer presenting: A paper ☒, a poster session ☐

Title: Ottawa River Nuclear Spill Contingency Model Development - Phase II

Abstract:

The purpose of the Ottawa River spill model development is to allow contingency planning in the case of a nuclear (probably tritium) spill from the Rolphton nuclear power demonstration (NPD) facility. A model which stimulates the two-dimensional - downstream and cross-stream - flow of pollutant already exists in the form of the FORTRAN 77 program TWODIFIN. The purpose of the Phase II Study is to extend this program.

As part of the Phase II Study, a one-dimensional version of the spill model has been developed and implemented in the computer program ONEDIFIN. This is a one-dimensional model - that is, it treats the river as a one-dimensional line and thus assumes complete lateral mixing of pollutant - that can be used to speed up calculations when the pollutant is laterally well-mixed. It is a multiple-source model, so that it can handle simultaneous spills from different locations, and it allows for first-order decay of the radioactive material.

Another major part of the Phase II Study was to interface the one- and two-dimensional programs. In such a hybrid program, the two-dimensional model would be used only for the portion of river that is not laterally well-mixed. Elsewhere, the one-dimensional model would be used, increasing the speed and efficiency of the calculations. This program has been developed and exists in single- and multiple-source versions - ONETWO and OTMULT, respectively.

Along with the main modelling portions, the study also involved the development of computer graphics and other programs to make the model interactive and easy to use. This is proceeding and it is hoped that the graphics will play a major role in helping to analyze and deal with potential spills. Also, model calibration is being performed using field data from the 1981 tritium spill from the Rolphton NPD.

SESSION C

LIQUID & SOLID WASTE RESEARCH

ABSTRACT FORM

Author : E. Timothy Oppelt
Address : Thermal Destruction Branch, Alternative Technologies Div.,
U.S.-EPA, Cincinnati, Phone (513) 569-7696
Co-Authors : Ohio, 45268, U.S.A.

Topic Area : Air ☐, Water ☐, Waste ☒, Analytical ☐

Environmental Economics ☐

Do you prefer presenting: A paper ☒, a poster session ☐

Title: Hazardous Waste Destruction: An Overview of Approaches and Shortcomings

Abstract:

Since 1980, the U.S. Environmental Protection Agency (EPA) has conducted extensive research to assess the performance of hazardous waste thermal destruction processes. This research has been designed to support the development and implementation of regulations and standards for controlling the safe operation of thermal destruction facilities in the United States. While these studies have largely shown thermal destruction to be the most practical and effective technology available for ultimate control of organic hazardous waste materials, some members of the scientific and environmental action community remain concerned about the long-term safety of the technology. The issues most frequently raised pertain to the possibility that harmful levels of heavy metals and incomplete combustion by-products may still be emitted from thermal destruction facilities that are otherwise meeting the current RCRA standards. The lack of available real-time monitoring techniques for tracking thermal destruction efficiency and detecting possible process upsets adds to the uncertainty and perceived risks associated with facility operation.

This paper will summarize the most recent data on thermal destruction facility performance with particular attention to metal and organic by-product emissions. Ongoing EPA research in this area and in real-time monitoring will be discussed. Real versus perceived concerns over thermal destruction will be put in perspective.

ABSTRACT FORM

Author : Norbert B. Schomaker
Address : Hazardous Waste Engineering Research Lab., US-EPA,
Cincinnati, Ohio, U.S.A.Phone ( )
Co-Authors :

Topic Area : Air ☐, Water ☐, Waste ☒, Analytical ☐
Environmental Economics ☐

Do you prefer presenting: A paper ☒, a poster session ☐

Title: U.S. E.P.A. Research on Land Disposal of Hazardous Waste.

Abstract:

The Land Pollution Control Division (LPCD), Hazardous Waste Environmental Research Laboratory (HWERL), U.S. Environmental Protection Agency, in Cincinnati, Ohio, has responsibility for research in solid and hazardous waste management with respect to land disposal of wastes. To fulfill this responsibility, the LPCD is developing concepts and technology for new and improved control systems for solid and hazardous waste land disposal; is documenting the environmental effects of various waste disposal practices; and is collecting data necessary to support implementation of disposal guidelines mandated by The Hazardous and Solid Waste Amendments of 1984 (HSWA). This paper will present an overview of the land disposal research associated with the LPCD hazardous waste program plan and will report the current status of work in the following categorical areas:

A. Hazardous Waste Facilities - Landfills and Surface Impoundments
    1. Cover Systems
    2. Waste Leaching/Modification
    3. Flexible Membrane Liners
    4. Clay Soil Liners
    5. Quality Assurance/Quality Construction
    6. Expert Systems
    7. Corrective Action

B. Non-Hazardous Waste Facilities
    1. Subtitle "D" Facilities

C. Technology Transfer
    1. Technical Research Documents

ABSTRACT FORM

Author : S.J. Thorndyke
Address : Ontario Research Foundation
Mississauga, Ontario Phone (416) 822-4111
Co-Authors : L5K 1B3

Topic Area : Air ☐, Water ☐, Waste ☒, Analytical ☐

Environmental Economics ☐

Do you prefer presenting: A paper ☒, a poster session ☐

Title: Assessment of a Prototype System For Pyrolysis of Refuse Derived Fuel

Abstract:

EFW Systems Incorporated have developed and constructed a prototype unit to pyrolyse refuse derived fuel (RDF), with the intent of using the pyrolysis gases as an engine fuel to generate electricity and as a source of process heat for the pyrolyser. An environmental and process assessment of the prototype unit has been made to determine potential advantages and disadvantages of the system in comparison to conventional municipal solid waste (MSW) incineration techniques.

The sampling and analytical program is briefly discussed, covering process operating conditions, emission components of interest, sampling and analytical methodologies and problems encountered. Data are presented to show the impact on air quality if pyrolysis gases were emitted directly to the atmosphere, and the potential problems for unit operators resulting from pyrolysis gas leakages. An approximate energy balance for the system shows that process modifications would be required to have pyrolysis gas available as an engine fuel.

ABSTRACT FORM

Author : G.W. Carter
Address : Resorption Canada Ltd., 2465 Stevenage Drive, Ottawa,
Ontario, K1G 3W2 Phone (613) 526-1400
Co-Authors :

Topic Area : Air ☐, Water ☐, Waste ☒, Analytical ☐

Environmental Economics ☐

Do you prefer presenting: A paper ☒, a poster session ☐

Title: Municipal Solid Waste Feasibility of Gasification with Plasma ARC

Abstract:

Resorption Canada Limited (RCL), in conjunction with Ontario Hydro Research Division and OBOE Engineering Limited, is conducting a feasibility study of the plasma gasification of Municipal Solid Waste (MSW), including operational experimentation within the RCL Plasma Research Facility in Ottawa, Ontario. The objectives of the study are to demonstrate the operational and environmental characteristics of the plasma gasification of MSW in order to increase the visibility and potential acceptability of the use of plasma technology in such an application.

This experimentation is expected to largely substantiate the postulated process characteristics of plasma gasification of MSW, the most salient of which include: a 4-5 fold increase in usable output energy compared to input electrical energy which represents a theoretical recovery of approximately 95% of the available energy in the input material, a product gas with a potential heating value of 300-350 BTU/scf, and a potential minimal requirement for environmental controls for the subsequent combustion of the product gas or the disposal of the virtually inert byproduct slag. The major benefits considered achievable through the plasma gasification of MSW are: more flexibility of potential operation since the output is a product gas; lower capital costs due to greater potential integration of the process equipment into an owner's existing facility; the minimization of undesirable pollution products in the product gas and the maximization of the energy recovered from the input material since both the operating temperature and the heat transfer rate are variable virtually at will; the complete breakdown of the input material and the production of smaller molecules which are inherently less hazardous; the processing of input material at any rate from next to nothing up to the maximum capacity of the system, all at the optimal operating point; the minimization of pollutants exhausted to the atmosphere since the material must first pass through two chemical reactions before being exhausted; and, a potential commercial market for the virtually inert byproduct slag.

Stage 1 of the project, which will determine the Higher Heating Value (HHV) of the product gas and the total process heat balance, commenced 1 April 1986. Stage 2, which will determine the environmental acceptability of the process and the subsequent combustion of the product gas is scheduled for commencement early in 1987 dependent on the results obtained through Stage 1. Project costs are being shared by the project participants, Plasma Energy Corporation of Raleigh, North Carolina and the Ontario Ministries of Energy and Environment.

ABSTRACT FORM

Author : J.L. Eggens
Address : University of Guelph, Dept. of Horticultural Science
Guelph, Ontario, N1G 2W1 Phone (519) 824-4120
Co-Authors :

Topic Area : Air ☐, Water ☐, Waste ☒, Analytical ☐
Environmental Economics ☐

Do you prefer presenting: A paper ☒, a poster session ☐

Title: Sewage Sludge Compost as Turf Fertilizer

Abstract:

The suitability of the Windsor composted fertilizer for Turf has been evaluated on home lawn-type turf (primarily *Poa pratensis*) at the Horticultural Research Station at Cambridge and on fairway turf (mixed *Poa annua* and *Agrostis palustris*) at the Weston Golf and Country Club, Weston, Ontario. At both locations, Turf fertilized with the Windsor material was as good as turf fertilized with a urea-based fertilizer. At the Cambridge site, the Windsor material performed as well as Milorganite. There appeared to be no difference in thatching tendency, susceptibility to drought or disease, in turf color or turf growth. On the golf course fairway, the speckling commonly note with urea was not evident with the Windsor material. A *Poa Annua* sward has been established at the Cambridge site to evaluate the response of this species to the Windsor material and Milorganite during 1987.

ABSTRACT FORM

Author : Ramesh Makhija
Address : Dept. of Chemistry, Trent University
Peterborough, Ontario Phone (705) 748-1298
Co-Authors : Robert A. Stairs

Topic Area : Air ☐, Water ☐, Waste ☒, Analytical ☐

Environmental Economics ☐

Do you prefer presenting: A paper ☒, a poster session ☐

Title: Waste Management Planning for Pharmaceutical Industry
Phase I, Inventory and Data Collection

Abstract:

The survey of waste generated by the pharmaceutical industry in Ontario is almost complete. The questionnaire originally prepared by the Ministry was modified, and was sent to approximately 70 establishments (manufacturers, hospitals and distributors). We have received responses from a little over 60% of the recipients. On the basis of replies received, it is apparent that most wastes are incinerated or sent to landfill. Notable quantities are, however, going to municipal sewers, including some psychotherapeutics, corticosteroids, and biologicals. These are being further investigated. The paper will discuss these and other findings in some detail, our tentative recommendations and plans for further work.

ABSTRACT FORM

Author : G. Zukovs
Address : 75 The Donway West, Suite 1014
Don Mills, M3C 2E9 Phone (416) 445-0434
Co-Authors :

Topic Area : Air ☐, Water ☐, Waste ☒, Analytical ☐
Environmental Economics ☐

Do you prefer presenting: A paper ☒, a poster session ☐

Title: Development of Guidelines for the Utilization of Industrial Waste In Backfill and Construction Applications.

Abstract:

The proposed evaluation guideline used to assess the suitability of industrial waste materials for various backfill and construction options will be presented. The rationale underlying the guidelines will be reviewed and the specific bulk material and leachate quality criteria for various disposal/utilization options will be detailed. Specific criteria will be presented for the following options:

- Lakefill/Shoreline Disposal
- Unrestricted Land Disposal
- Restricted Land Disposal
- Construction Applications

The second portion of the paper will review available Ontario data obtained from literature sources dealing with the bulk and leachate quality of the following waste materials:

Coal Ash - flyash, bottom ash
Foundry Wastes - slags, foundry sands,
foundry dusts, foundry sludges
Sewage Sludge Incinerator Ash
Cement Kiln Dust

ABSTRACT FORM

Author : G.J. Farquhar
Address : Civil Engineering, University of Waterloo
Waterloo, Ontario Phone (519) 885-1211, ext. 3349
Co-Authors : E.A. McBean, J.M. Byrne, W. Abbott and R. Kell

Topic Area : Air ☐, Water ☐, Waste ☒, Analytical ☐

Environmental Economics ☐

Do you prefer presenting: A paper ☒, a poster session ☐

Title: Numerical and Laboratory Modelling of Two-Phase Flow in Porous Media: 1. Two-phase gaseous flow. II. Two-Phase Liquid Flow.

Abstract:

Numerical and laboratory modelling of two-phase fluid flow in porous media is taking place under a larger project "Assessing the Impact of Hazardous Liquids spilled onto Soil." Numerical models to simulate two-phase liquid and vapour situations have been developed, and early verification against laboratory data has produced very good results. Liquid phase experiments are monitoring the migration of an immiscible liquid through a sixty cm. water-saturated vertical sand column. Relative liquid saturation behind the intruding front is monitored to steady-state with the thermal conductivity probe developed at UW. Relative permeability curves as a function of oil and water relative saturations have been developed.

Two phase gaseous flows are being modelled in a 4 x 1.3 x 0.3 metre sandbox. Hexane liquid is introduced in a pan and allowed to volatilize and migrate away from the source. Numerical and laboratory results are compared to determine soil absorption properties and variabilities in the parameters governing hazardous diffusion in porous media.

ABSTRACT FORM

Author : J.J. Ganczarczyk
Address : Dept. of Civil Engineering, University of Toronto
Toronto, M5S 1A4 Phone (416) 978-3141
Co-Authors :

Topic Area : Air ☐, Water ☐, Waste ☒, Analytical ☐
Environmental Economics ☐

Do you prefer presenting: A paper ☒, a poster session ☐

Title: Development of Plysulfide Technology for Treatment of Concentrated Spent Cyanide Liquors.

Abstract:

The polysulfide reaction offers a possibility for a simple effective, and inexpensive pre-treatment of concentrated spent cyanide liquors which are a troublesome byproduct of electroplating. The feasibility of such pre-treatment has been confirmed in previous studies but several technological questions remained unanswered.

In this study extensive tests on spent plating solutions of various concentrations and origin have been performed with an application of calcium and sodium polysulfide. The purpose of these experiments was to establish the reliability of the process and its optimal conditions.

To eliminate possible problems with supply of commercial grade calcium polysulfide in bulk quantities, and at a reasonable price, experiments have been carried out on an on-site production of polysulfide agent from lime and sulfur. A preliminary economical evaluation of such a production has been formulated.

The sludge generated during the polysulfide reaction with the spent liquors has been characterized under laboratory scale conditions. More tests in a pilot scale are intended.

ABSTRACT FORM

Author : R. McBride
Address : Land Resource Science; Environ. Biology
Univ. of Guelph Phone (519) 824-4120, x. 2492
Co-Authors : A.M. Gordon, P. Groenvelt, T. Bates and K. King

Topic Area : Air ☐, Water ☐, Waste ☒, Analytical ☐

Environmental Economics ☐

Do you prefer presenting: A paper ☒, a poster session ☐

Title: Treatment of Landfill Leachate by Spray Irrigation - Muskoka Lakes

Abstract:

This research addresses present and potential problems arising from the installation of a spray irrigation system designed to concentrate leachate from the Muskoka Lakes Landfill onto a nearby forested area of mixed hardwoods. The forest is now showing severe mortality in areas where spraying has been previously concentrated. A brief summary of past and ongoing activities is presented.

Surface and subsurface hydrological investigations have been undertaken with a view to reducing the volume of leachate being generated from the estimated current mean rate of about 60,000 $1.\text{day}^{-1}$. Feasibility studies are underway to investigate practical means of reducing i) the infiltration of incident precipitation through the landfill cover and ii) the extent of groundwater contact with landfilled refuse.

The ability of the local soils to attenuate spray irrigated leachate is being studied in the field via soil water regime characterization and soil solution/groundwater sampling, and in the laboratory with intact soil leaching columns.

Time sequenced infra-red aerial photography is being used to monitor the severity of perceived stresses imposed on the mixed hardwood forest ecosystem through the growing season. More precise field measures of transpiration rate and vegetative growth depression are being made with a porometer and increment bore/foliar nutrient sampling, respectively. Influences of leachate spraying on soil microbial biomass and respiration are also being ascertained. The latter employs a soda-lime CO_2 absorption field assay. A greenhouse experiment utilizing red and sugar maple seedlings, subjected to foliar and soil applications of untreated, lime-treated, and activated carbon-treated leachate will assist in further isolating the nature of the vegetative stresses apparent in the forest from past spraying sequences.

ABSTRACT FORM

Author : D.W. Kirk
Address : Dept. of Chemical Engineering, University of Toronto
200 College Street Phone (416) 978-7406
Co-Authors : M. Lau

Topic Area : Air ☐, Water ☐, Waste ☒, Analytical ☐

Environmental Economics ☐

Do you prefer presenting: A paper ☒, a poster session ☐

Title: Co-Disposal of Industrial and Municipal Wastes. Part II.

Abstract:

This work is part of a longer term study of factors involved in the mobilization of metal species from solids contained in a landfill environment. Current methods of testing for the suitability of solids for disposal in municipal landfill sites do not take into account the anaerobic environment generated by microbial action or the role of biological metal mobilization, and thus the screening tests may not provide the appropriate information required.

In an earlier report the standard EP leach test for a steel flue gas dust was compared with modified leach tests with mixed municipal refuse and the steel flue gas dust. In this report, results form experimental landfill test columns are presented. The columns are designed to provide data on metal mobilization within a municipal refuse landfill with and without various loadings of the steel flue gas dust. Both atmospheric and controlled water input are compared.

The results of the work show that the presence of the industrial waste has a beneficial effect in inhibiting the release of many metal species over the timeframe studied.

ABSTRACT FORM

Author : J.F. Barker
Address : Dept. of Earth Sciences, University of Waterloo
Waterloo, Ontario Phone (519) 885-1211, ext. 2103
Co-Authors : Cherry, J.A.

Topic Area : Air ☐, Water ☐, Waste ☒, Analytical ☐

Environmental Economics ☐

Do you prefer presenting: A paper ☒, a poster session ☐

Title: Hazardous Organic Chemicals in Groundwater at Ontario Landfills

Abstract:

Studies have been conducted at five landfills in Ontario ranging in latitude from the North Bay landfill in the north to a landfill near Sarnia in the south. The sites represent a variety of geologic materials in which migration of leachate-derived contaminants occurs, including sand aquifers, sandy silty glacial till, clayey glacial till and fractured shale. With the exception of the clayey till site, at each of the sites extensive lateral migration (200 m   1000 m) of organic contaminants, particularly the common volatile organics, has taken place. These landfills range in age from one to three decades. The total dissolved organic carbon in the contaminated groundwater is generally in the range of 10 to 200 mg/L. The total load of identifiable organic compounds is only a small fraction of this total. The nature of the suite of characteristic volatile organics differs considerably from landfill to landfill, and to some degree reflects the nature of the industrial base of the municipality. The spatial distribution of volatile organics within each plume is generally much more complex than the distribution of the standard plume indicator parameters such as total dissolved solids, electrical conductance, total dissolved organic carbon and chloride. The design of effective monitoring networks for trace organic contaminants is therefore more difficult. At the landfill on clayey glacial till, the downward migration of Cl- and volatile organic compounds was determined through work done in collaboration with the Oregon Graduate Center. Vertical cores were collected from the bottom of a five year old hazardous waste-disposal pit in unweathered clayey material. These cores show that downward contaminant migration has occurred due to molecular diffusion without significant influence of groundwater flow. Chloride has diffused 85 cm in 5 years. Volatile organic compounds have moved at a slow rate due to adsorption. The clayey till below the pit site is 26 m thick and therefore the aquifer below is not threatened. In a different context, however, the results indicate that molecular diffusion is a process that will cause contaminants to move through compacted clay liners relatively quickly even if the liners achieve a very low permeability.

ABSTRACT FORM

Author : I. Proulx
Address : Institute for Groundwater Research
Univ. of Waterloo Phone (519) 885-1211 ext. 6256
Co-Authors : R.N. Farvolden, E.O. Frind

Topic Area : Air ☐, Water ☐, Waste ☒, Analytical ☐

Environmental Economics ☐

Do you prefer presenting: A paper ☒, a poster session ☐

Title: Dispersion of the Stouffville Contaminant Plume

Abstract:

The quality of groundwater in the Oak Ridges aquifer complex underneath the Stouffville landfill site has been monitored since 1968. Data on many chemical parameters allow dilineation of the contaminant plume, and assessment of its evolution with time.

Previous work has identified a thick unsaturated zone occurring above the aquifer, with perched groundwater in the overlying Halton till. Numerous ponds present in the area suggest that little recharge takes place areally through the till. A recent IGR study in the Musselman lake area, immediately upgradient of the site, has described the recharge characteristics of the aquifer. A computer model to represent the groundwater flow is now applicable.

Present work aims at gaining more information on the physical properties of the glacial outwash forming the acquifer, in order to enable a characterization of the strength of the dispersion process. Focus is on the degree of heterogeneity and the spatial arrangement of the hydraulic properties.

ABSTRACT FORM

Author : L. Arnaud

Address : Institute for Groundwater Research
Univ. of Waterloo Phone (519) 885-1211 ext. 3960

Co-Authors : E.O. Frind, R.N. Farvolden, R.W. Gilham

Topic Area : Air ☐, Water ☐, Waste ☒, Analytical ☐

Environmental Economics ☐

Do you prefer presenting: A paper ☒, a poster session ☐

Title: Development of Design Criteria for Optimal Recovery of Leachate Under Sanitary Landfills.

Abstract:

A two-dimensional finite element model was used to study the effectiveness of tile drain systems for capturing leachate escaping from sanitary landfills. Computed steady-state conditions were compared with data produced from a laboratory model with a homogeneous and isotropic sand medium. Simulations were conducted for single drain configurations with varying vertical hydraulic gradients, drain depth, thickness of the flow field, drain spacing and recharge rate. Results showed that most of the fluid or leachate could be collected if an upward gradient existed between the drain level and the bottom of the system. If the gradient was downward, the drains had to be very closely spaced in order to collect the fluid. Drain performance depended also on the rate of recharge to the system. The amount of recharge controlled, in part, the height of the groundwater mound between the drains. Optimum conditions were attained when all the leachate was collected with minimum infiltration from the underlying hydrogeological unit.

The numerical model was also used to verify the influence of a network of drains on regional groundwater flow. Resulting flownets illustrate the influence of regional horizontal gradients, recharge, thickness of the aquifer, and drain depth on the amount of water collected. For homogeneous and isotropic systems, the influence of the drains can be observed deep inside the flow field.

Numerical simulations were performed for cases of anisotropy in the porous medium and for cases having a less permeable layer of varying depth, thickness, and relative hydraulic conductivity. These results show that anisotropy and heterogeneity can affect significantly the performance of a given drain system design.

Both systems under study (single drain and regional) are useful to evaluate the role of tile drains as leachate and groundwater collectors.

ABSTRACT FORM

Author : Linda Elliott
Address : Box 430 Carp, Ontario, KOA 1LO
Phone (613) 836-2594
Co-Authors : J.F. Devlin, F. Michaels, and W.A. Gorman

Topic Area : Air ☐, Water ☐, Waste ☒, Analytical ☐

Environmental Economics ☐

Do you prefer presenting: A paper ☒, a poster session ☐

Title: An Investigation Into The Redox Conditions Of A Landfill Leachate Plume Containing Volatile Organics, Gloucester, Ontario

Abstract:

Recent research has indicated that the rate of degradation of volatile organic compounds in ground water is dependent on the existing redox conditions. In general, aromatic compounds degrade most quickly under aerobic conditions while aliphatic compounds are most quickly degraded under anaerobic conditions. A detailed redox survey was carried out at the Gloucester Landfill site, Gloucester, Ontario, in 1985, to establish the redox conditions within a contaminant plume containing volatile organics. The redox conditions at 129 sampling points throughout the plume were characterised three ways: (1) EH measurements were made using a platinum electrode connected to a flow cell. PH and temperature probes were also connected to the flow cell so that all three field measurements could be recorded at the same time; (2) dissolved oxygen measurements were carried out with a second, independent, flow cell; (3) field and laboratory measurements of sulfate and sulfide concentrations in the ground water were carried out. These values were used to calculate a Nernstian "pe" for each sampling location. A concurrent study into the distribution of volatile organics on the site provided the contaminant data.

EH measurements made with a platinum electrode were found to be very imprecise. It is recommended that in future studies they be used only as a reconnaissance tool. Dissolved oxygen measurements and "pe" calculations were found to best delineate aerobic and reducing environments, respectively.

The possibility that redox controlled chemical and/or biologically mediated transformations are taking place at the site will be addressed by identifying possible parent and daughter compounds and examining their distributions within the reducing and oxidizing environments.

ABSTRACT FORM

Author : R.M. Quigley
Address : Geotechnical Research Centre, Faculty of Engineering
Univ. of Western, Ont. Phone (519) 661-3344
Co-Authors : Fernandez, F.

Topic Area : Air ☐, Water ☐, Waste ☒, Analytical ☐
Environmental Economics ☐

Do you prefer presenting: A paper ☒, a poster session ☐

Title: Effects of Increasing Amounts of Non-Polar Organic Liquids in Domestic Waste Leachate on the Hydraulic Conductivity of Clay Liners in Southwestern Ontario.

Abstract:

Organic liquids, less polar than water, are capable of producing dramatic changes in the structure of clayey soils and their hydraulic conductivity. Double layer theory is adequate to explain the behaviour of pure liquid-clay mixtures, however, it fails to account for the behaviour of water-compacted clays sequentially permeated by water and organic liquids. The "hydrophobic" nature of non-polar liquids such as cyclohexane and benzene, restricts their flow to larger channels through the pore system, resulting in decreases in k and with little effect on the double layers of water. The values of k seem to be dependent on the hydraulic gradient applied (non-Darcian behaviour) and threshold gradients may be measured below which breakthrough a flow do not occur. Viscosity plays an important role on the behaviour of water-soluble permeants such as ethanol and dioxane, producing an initial decrease followed by gradual increases in k to equilibrium values that are practically independent of the hydraulic gradient used.

The addition of organic liquids induced rapid flocculation of the otherwise stable suspended matter in domestic waste leachate, the rate of flocculation being more pronounced with increasing abundance of organic liquids. Inorganic salts also precipitated resulting in a decrease in salinity of the clear leachate phase. The physical location of the floccs (as floaters or sinkers) depends on the amount and type of organic liquid added.

Preliminary testing on water-compacted brown Sarnia soil using the clear phase of domestic leachate containing up to 45% ethanol and 5% benzene has yielded no significant increases in k. Furthermore, leachate spiked with 20% ethanol produced a decrease in k that is believed to be due to its higher viscosity.

Solubility limits mean that large amounts of most non-polar organics will generally produce two liquid phases. Additional testing will be presented showing the results of k testing at high and low organic contents. Special tests using non-polar but totally water-soluble dioxane will also be presented.

ABSTRACT FORM

Author : M. Dickman
Address : Brock University, St. Catharines, Ontario
L2S 3A1 Phone (416) 688-5550 Ext. 3392
Co-Authors : Ian Brindle, Chemistry Dept., Brock University

Topic Area : Air ☐, Water ☐, Waste ☒, Analytical ☐
Environmental Economics ☐

Do you prefer presenting: A paper ☒, a poster session ☐

Title: Assessment of Contaminant Migration from Industrial Sources Dicharging to the Welland River

Abstract:

A team of 3 chemists, 3 aquatic toxicologists, 2 genetic toxicologists, 3 environmental studies scientists, 2 field workers and 1 project coordinator collected and tested samples from the Welland River below major industries. The impact which these effluents had on the first, invertebrates and aquatic vegetation of the Welland River was described in terms of four biological zones: 1) Impact zone, 2) Primary Recovery zone, 3) Secondary Recovery zone and 4) Tertiary Recovery zone.

Chemical analyses of the effluents and the receiving waters and their sediments was correlated with the zonation pattern described above. In general, the larger the area of the impact zone the more toxic the effluent. Chromotoxicity and Ames testing of the effluent and sediments of each source was also conducted. Preliminary chemical analyses confirmed a definite relationship between contaminant levels and the effects on the Welland River biota.

Continuous specific conductivity tests of the effluents form selected industries revealed with sporadic discharges (shock loads) of electrolytes were entering the Welland River. When the biotoxicity testing was performed using effluent discharged during these shock loading events the biotoxicity was far higher than when effluent displaying background conductivity levels was used. When thee data were provided to one of the industries in this study a cooperative program was established. In this case the industry actively solicited the cooperation of our investigative team in pin-pointing the source of its shock load discharges. The source as traced to their Vacuum Oxygen Refining System which has now been renovated to prevent shock loading to the River. This work has established the precedent for cooperative toxicological research between industries on the Welland River and our investigative team at Brock University.

ABSTRACT FORM

Author : J.A. Cherry
Address : Institute for Groundwater Research
University of Waterloo Phone (519) 888-4516
Co-Authors : E.A. Sudicky and R.J. Blackport

Topic Area : Air ☐, Water ☐, Waste ☒, Analytical ☐
Environmental Economics ☐

Do you prefer presenting: A paper ☒, a poster session ☐

Title: Evaluation of Contaminant Velocity Groundwater in Low-Permeability Fracture Shale.

Abstract:

This study, which began in August 1985, focuses on methods for determination of velocity and, to a lesser degree, dispersion in fractured shale. Emphasis is placed on bedrock shale in the Burlington-Oakville region. Shale in this region is important because it occurs at or very near ground surface in many areas where landfilling or industrial activities take place. The shale is not very permeable but nevertheless groundwater velocity can be relatively high in some zones. This study involves detailed field tests at a field site in Oakville (a second field site may be selected in the second year of this project). Field results are being used to develop improved modeling approaches for flow and contaminant migration in the shale. At the field site cored boreholes have been drilled, specific zones of fractures have been identified and hydraulic testing using two types of borehole packer equipment have been identified and hydraulic testing using two types of borehole packer equipment have been performed. Larger scale tests to determine the hydraulic continuity of fracture zones are in the planning stage.

ABSTRACT FORM

Author : M.B. Dusseault
Address : Dept. of Earth Sciences, University of Waterloo
Phone (519) 885-1211
Co-Authors : A.G. Vorauer

Topic Area : Air ☐, Water ☐, Waste ☒, Analytical ☐
Environmental Economics ☐

Do you prefer presenting: A paper ☒, a poster session ☐

Title: Geomechanical Investigation of Near-Surface Fractures in Clay Tills: Part 2: Laboratory Investigation of Strength and Mineralogy

Abstract:

Three sites were chosen across southwestern Ontario for the purpose of studying the characteristics of the near-surface weathered and unweathered zone in the clays and clay tills. In an attempt to determine the regional characteristics of these altered sediments, the sites were selected as to represent three distinct geomorphological areas found across southwestern Ontario: 1) the Nanticoke site located in the varved lacustrine Haldimand clays, 2) the London site located on Port Stanley till, 3) the Essex site located on the "water-laid" tills of the St. Clair clay plains region.

The first part of this study dealt with the fracture patterns and fracture-forming mechanisms observed at each site. This laboratory portion of the study has made use of 4 inch diameter Shelby tube samples collected from the weathered and unweathered zones. Standard geotechnical characterization tests were performed such as grain-size analysis, Atterberg limits and oedometer consolidation tests. A series of multi-stage, consolidated-undrained triaxial tests were also performed to determine differences in stress-strain behaviour between the weathered and unweathered sediments, as well as the lacustrine clay and till deposits. Tensile strength tests using laboratory hydraulic fracture were also attempted on the intact and fractured clay samples to complete their geomechanical characterization.

The mineralogy of the weathered and unweathered zones, as well as the fracture infilling material, were determined using standard X-ray diffraction techniques.

This paper concludes with a discussion on the laboratory strength and mineralogy of the near-surface clays and clay tills found in southwestern Ontario and how these characteristics have been altered through the weathering process. The implication of these changes upon the siting, construction and long-term behaviour of waste management facilities located on clay deposits are examined.

ABSTRACT FORM

Author : P.E. Pilon
Address : University of Toronto, Scarborough Campus
Phone (416) 284-3336
Co-Authors : K.W.F. Howard

Topic Area : Air ☐, Water ☐, Waste ☒, Analytical ☐

Environmental Economics ☐

Do you prefer presenting: A paper ☒, a poster session ☐

Title: Origins of Elevated Chloride Concentrations in Groundwater Systems

Abstract:

Shallow aquifer systems in southern Ontario frequently exhibit elevated chloride concentrations that locally exceed water quality guidelines. While in some cases the elevated chloride concentrations can be attributed to indigenous sediment sources, more commonly they are introduced by external point and non-point sources of both natural and man-made origins. Natural origins primarily include formation waters resident in underlying Paleozoic sediments; manmade origins are numerous and include road de-icing chemicals, inorganic fertilizers, urban development, landfills, septic tanks, and animal feedlots.

At the University of Toronto, hydrochemicl studies are in progress that aim to develop multi-parameter methods of identifying sources of groundwater contamination. Chemical parameters have included major ions (Ca, Mg, Na, K, Cl, SO_4, NO_3 and HCO_3, minor ions (Br, I, and F), and over 20 trace metals. Tritium has been used locally. To date the study has focused on road de-icing chemicals, saline bedrock waters, fertilizers and urban development as the primary external sources of the chloride enrichment. A total of 110 domestic well water samples, 40 contaminant samples and 70 interstitial water samples have been collected and analyzed.

Much of the completed work has been aimed at determining the natural background levels of major, minor and trace chemical constituents in naturally evolving uncontaminated groundwaters. In addition attempts have been made to characterize chemically the major sources of contamination in the area and, more importantly, to develop an understanding as to how the chemical characteristics of the contaminants are modified during transport through the shallow sub-surface. In general, the minor inorganic anions (I, Br and F) have provided to be the most reliable indicators of chloride origin, being particularly effective at distinguishing between bedrock and road de-icing chemicals as sources of saline wter. Although relatively few of the trace metals have shown anomalously high concentrations in the chloride enriched groundwaters, there are strong indications that A1, Ni, Ba, Cu, Zn and Pb may prove beneficial indicators of contaminant origin in specific situations.

SESSION D

ANALYTICAL METHODS

ABSTRACT FORM

Author : J.B. French
Address : Institute for Aerospace Studies, University of Toronto
Phone (416) 667-7780
Co-Authors :

Topic Area : Air ☐, Water ☐, Waste ☐, Analytical ☒
Environmental Economics ☐

Do you prefer presenting: A paper ☒, a poster session ☐

Title: Trends in Multielement Analysis:
The Role of ICP/MS in Environmental Applications

Abstract:

This review paper assesses the trends in multielement analysis in major environmental laboratories, in terms of the forces shaping these trends and the evolving instrumentation capabilities. Legislation and legal requirements, public awareness, and industrial monitoring requirements are all seen as increasing the need for (1) multielement trace component analysis at ever-decreasing concentrations (2) capability of handling large increases in the number of determinations per day in the most cost-effective manner possible (3) unimpeachable, legally defensible data. The present capabilities of x-ray diffractometers, flame and furnace atomic absorption spectrometers, and plasma atomic emission spectrometers are reviewed and compared to the capabilities of the newer induction coupled plasma/mass spectrometers (ICP/MS). Stability, precision and sample matrix effects are also reviewed in terms of proven and emerging capabilities.

ICP/MS instruments are seen to combine in one instrument parts per billion detector limits with large sample volume throughput and trace multielement capabilities. Additionally, results are reviewed which show that they can usefully determine isotopic ratios, and the future importance of this dimension to environmental work is discussed. Examples of application to environmental studies of river water, continental aquifers, estuarial samples, acid rain effects and lead pollution are reviewed. The tend toward more versatility in sample pretreatment and introduction methodologies is discussed together with the implications for better environmental sample handling and utilization.

ABSTRACT FORM

Author : Marcia G. Nishioka and Corrine C. Howard
Address : Analytical Chemistry Section, Battelle Columbus Division
Columbus, Ohio, 43201 Phone ( )
Co-Authors : Joellen Lewtas, US-EPA, North Carolina

Topic Area : Air ☐, Water ☐, Waste ☐, Analytical ☒

Environmental Economics ☐

Do you prefer presenting: A paper ☒, a poster session ☐

Title: Detection of Hydroxylated Nitro-Polynuclear Aromatic Hydrocarbons and Ketones in an Ambient Air Particulate Extract Using Bioassay-Directed Fractionation.

Abstract:

The identification of hydroxylated nitro-polynuclear aromatic hydrocarbons ($OH-NO_2$-PAHs) and hydroxylated nitro-polynuclear aromatic ketones ($OH-NO_2$-PAKs) in an ambient air particulate extract by electron impact (EI) and negative chemical ionization (NCI) high resolution gas chromatography/mass spectrometry (HRGC/MS) analyses is presented here. Bioassay-directed fractionation through three sequential separations led to detection of these $OH-NO_2$-PAHs/PAKs in a highly mutagenic and substantially simplified subfraction of the extract. The compound class identification was based on comparison of both EI and NCI mass spectra of reference $OH-NO_2$-pyrenes. The HRGC/MS retention values for nine $OH-NO_2$-pyrene isomers indicated that one of the compounds detected may be an $OH-NO_2$-fluoranthene isomer. Quantification of this compound class by NCI HRGC/MS, on-column injection, full scan acquisition is demonstrated with sensitivity to 0.5 ng/ml.

ABSTRACT FORM

Author : Eric D. Salin
Address : Dept. of Chem. McGill Univ., 801 Sherbrooke Street West
Montreal, P.Q., H3A 2K6 Phone (514) 392-5784
Co-Authors : R.L.A. Sing

Topic Area : Air ☐, Water ☐, Waste ☐, Analytical ☒
Environmental Economics ☐

Do you prefer presenting: A paper ☒, a poster session ☐

Title: Direct Solid Sample Analysis with the Direct Sample Insertion Device, Promise and Problems

Abstract:

The spectrometer and data acquisition requirements for solid sample analysis with the direct sample insertion device (DSID) will be discussed with respect to speed and background correction. The DSID requires a multichannel spectrometer for multielement analysis, however the rapid spectral background correction requirements drastically limit the selection of both the wavelength correction scheme and manufacturer. The results of preliminary work in our and other laboratories will be presented. Investigations of marine sediment samples have demonstrated detection limits which are sufficiently low to permit the detection of some elements at the sub ug/g level. The reproducibility of the signal for the marine sediments is poor and is suspected to be due to the inhomogeneity of the sample and the small sample size (2 mg). Other laboratories have succeeded in obtaining reproducible signals from larger samples (10 mg) of graphite, silicon dioxide and aluminum oxide based standards. Common linear calibration curves have been obtained for these standards. The use of other sample supports such as metal cups will be discussed as well as the use of Oxygen - Argon mixtures and halogen mixtures. The potential as well as the application of fluxes will be demonstrated for the generation of conditions suitable for sample breakdown.

ABSTRACT FORM

Author : Jon C. Van Loon
Address : Institute for Environmental Studies, University of Toronto
Phone (416) 978-5612
Co-Authors : B. French

Topic Area : Air ☐, Water ☐, Waste ☐, Analytical ☒
Environmental Economics ☐

Do you prefer presenting: A paper ☒, a poster session ☐

Title: Screening Methods for Air and Water Samples: Application of Inductively Coupled Plasma Mass Spectrometry (ICP/MS) to Elemental Analysis

Abstract:

Re Filament and graphite boat volatilizers (electrothermal vaporizers-ETV's) have been evaluated as sample introduction devices for ICP/MS. The elements studied to date include Cu, Cd, Ni, Fe, Pb, V, Sn, Au, P and Se. The Re filament can be used for the more volatile elements but elements such as V, Sn, P and Se are better handled using the graphite boat. Typical operational parameters for the Re filament are as follows: Ar flow 4.0 l/min, max T 1900°C, incident power to plasma 1.25 kW, sample size 2-5 L. The graphite boat can be used to about 2500°C. Calibration is by the method of standard additions. Both devices give up to 80% transport efficiency when a 5 to 10 ml volume exists in the glass dome above the filament (to allow aerosol condensation into microparticulate before it reaches the glass or tubing surface). Tangential Ar gas introduction is also used to aid minimization of aerosol interaction with ETV surfaces.

Detection limits using ETV sample introduction are up to 1.5 order of magnitude superior to those obtained on the same ICP/MS when cross flow nebulization is used. Ionization supression interference were minimized through ashing programs Mass spectral overlap was a problem when large amounts of Zn^{64} was present with Cu and Cu^{65}.

ICP source mass spectrometry has undergone preliminary investigation as a new mass specrometric detector for chromatography. The compounds separated by gas chromatography and detected were Me$_3$SnPe, Me$_2$SnPe$_2$ and MeSnPe$_3$. Introduction of O$_2$ into the gas flow from the GC was essential to prevent graphite build up in the torch. The use of O$_2$ also improves detection limits by 3 orders of magnitude.

ABSTRACT FORM

Author : Lewis M. Brown
Address : Dept. of Plant Sciences, University of Western Ontario,
London, Ont. N6A 5B7 Phone (519) 679-2111 x 6469
Co-Authors : John D. Wehr

Topic Area : Air ☐, Water ☐, Waste ☐, Analytical ☒

Environmental Economics ☐

Do you prefer presenting: A paper ☒, a poster session ☐

Title: Development of Selenium Analysis Methodology at Ng/L Levels for Soft Waters Subject to Acidic Precipitation

Abstract:

Our studies of nutritional factors important in controlling the composition of phytoplankton populations have indicated that some phytoplankton species in softwater lakes subjected to acidic precipitation require the element selenium for growth. Some of these phytoplanktons produce undesirable blooms. The levels of selenium required by these species is low. However, the meagre data available on Se concentrations in softwater lakes indicate that Se levels may be low enough to limit the growth of some phytoplankton, and that Se inputs from acidic precipitation, a known source of Se, may affect the composition of these communities. Because of the dearth of data on Se levels, it was decided to apply a sensitive method to analysis of this element in soft waters. In addition the known effects of Se in ameliorating some of the toxic effects of Hg suggest that Se may be important in soft waters for other reasons.

Atomic absorption methods as conventionally applied yield a detection limit in the ug/L range. This is inadequate for the studying the levels normally encountered in softwater lakes. A gas chromatographic method was applied and allowed detection at the low ng/L level. Several new features of this method have not been used previously in analysis of Se in natural waters. These include application of capillary chromatography to analysis of the piaselenol derivative (of 4-nitro-o-phenylenediamine) in soft waters, and a single flask derivatization procedure which considerably reduces handling and potential contamination. Retention time of the piaselenol peak was about 1.8 min with total analysis time of 5 min, at an operating temperature of 250°C. Preliminary data indicate that Se concentrations vary with season and depth and are typically less than 1 ug/L in softwater lakes. The method can also be used to study the distribution among the various species (Se-IV, Se-VI and organoselenium).

ABSTRACT FORM

Author : R.D. Evans
Address : Environmental and Resource Studies Program
Trent University Phone ( )
Co-Authors : Peterborough, Ontario

Topic Area : Air ☐, Water ☐, Waste ☐, Analytical ☒
Environmental Economics ☐

Do you prefer presenting: A paper ☒, a poster session ☐

Title: Evaluation and Optimization of a T.O.C.
Analyzer Utilizing U.V. - Persulphate Digestion

Abstract:

A series of tests were designed to evaluate the performance of a commercial total organic carbon analyzer which utilizes an automated UV-persulphate digestion. Initial tests explored the sensitivity, precision and accuracy of the machine. A practical lower limit of detection was approximately 0.5 mg C/L. One problem identified was the inability of the machine software to incorporate more than one calibration standard. As a result, some non-linearity was observed at the extremes of the calibration range.

Synthetic samples were prepared which incorporated a range of organic and inorganic carbon concentrations. These samples were analyzed in a double, blind test in comparison with traditional O.M.E. furnace techniques. The results of these tests indicate that, in general, U.V.-persulpahate digestion is capable of complete digestion and recovery of organic carbon. No systematic bias was found even in highly refractory samples such as isonicotinic acid. Paired "t-tests" between the two analytical methods revealed no significant differences between means.

The last phase of the study involved the comparison of various carbon fractions as measured with this technique with traditional determinations of organic content such as biological oxygen demand (BOD) and chemical oxygen demand (COD). Results of this phase of the study were variable. In some situations there was a good correlation between BOD and either total carbon or organic carbon but in most cases, the correlations were poor. As expected there was no correlation between inorganic fractions of carbon and oxygen demand. The results suggest that in some cases this instrument could be used as a fast screen for oxygen demanding wastes but further study is required to define the matrices for which the method is most applicable.

ABSTRACT FORM

Author : J.C. Van Loon
Address : University of Toronto, 170 College Street, Toronto
M5S 1A1 Phone (416) 978-5612
Co-Authors :

Topic Area : Air ☐, Water ☐, Waste ☐, Analytical ☒

Environmental Economics ☐

Do you prefer presenting: A paper ☒, a poster session ☐

Title: Development of an Ultrasonic Nebulizer for Stable and Reproductive Production of Aerosols for Atomic Spectrometric Analysis

Abstract:

The object of this work is to determine the feasibility of the construction and utilization of a relatively inexpensive but reliable ultrasonic nebulization system. The device should be applicable to the trace element analysis of environmental samples. The starting point for the investigation was a commercially available ($100) transducer/power supply used in a humidifier system. To date the majority of the research has involved design, modification and subsequent evaluations of suitable spray chamber-desolution atomizer equipment. Additionally modifications were found to be essential in the transducer power supply and housing systems. Research is now centering on methods of coating the transducer (as opposed to the usual and unreliable quartz plate bonded system) to obtained reproducible and reliable substrate form which to generate the sample aerosol. No useful quantitative results have yet been obtained.

ABSTRACT FORM

Author : W.C. Bradbury
Address : Toronto General Hospital, Dept. of Microbiology
Toronto, Ontario Phone (416) 595-4858
Co-Authors : M. Marko, L. Papageorgiou, D. Leicht and D. Rego

Topic Area : Air ☐, Water ☐, Waste ☐, Analytical ☒

Environmental Economics ☐

Do you prefer presenting: A paper ☒, a poster session ☐

Title: Development of Recombinant DNA Probes to Determine the Origin of Fecal Streptococci at the Toronto Area Beaches

Abstract:

Total cellular DNA from fecal Streptococci from goose, human and gull origin were digested with restriction endonucleases. The digestion patterns were grouped into families by visual inspection for commonality. An isolate from goose feces was chosen as a candidate for preparing the goose probe because this "family" included both sediment and fecal isolates.

The total cellular DNA was digested with the restriction endonuclease Bam HI and inserted into the Bam HI site of the cloning vector pUC 9. The colonies of E. coli which had been transformed by a recombinant plasmid were screened for plasmid content. The plasmids were digested with Bam HI and elecrophoresed in agarose gels. The DNA was transferred to millipore membranes and probed with 32P-labeled total cellular DNA from Streptococcus faecalis var liquefaciens of human origin. An insert of 6.6 Kb which did not hybridize to the probe was chosen as a candidate for the goose streptococcal DNA probe. This plasmid ws radiolabeled with 32P and used to analyze the total cellular DNA of fecal Streptococci of goose, human and gull origin. The probe hybridized to the "family" of goose fecal DNA from which it was derived and not the human fecal streptococcal DNA of non-lab workers. In addition only one of twenty (1/20) gull isolates reacted positively.

In a similar manner a probe for human fecal streptococcal DNA was generated from Streptococcus faecalis var liquefaciens of human origin and candidate recombinant plasmids were selected by their inability to hyrbidize with the total cellular DNA of Streptococcus var liquefaciens of gull origin. A plasmid with an insert of 2.0Kb was found to react with four of twenty (4/20) fecal streptococcal DNA of human origin but not with any of goose or full origin.

ABSTRACT FORM

Author : William F. Grant
Address : Genetics Laboratory, P.O. Box 4000, Macdonald College
McGill University Phone (514) 457-2000 ext. 379
Co-Authors :

Topic Area : Air ☐, Water ☐, Waste ☐, Analytical ☒
Environmental Economics ☐

Do you prefer presenting: A paper ☒, a poster session ☐

Title: Plant Bioassays for the Detection of Environmental Mutagens

Abstract:

It is well established that higher plants provide valuable assay systems for screening and monitoring environmental chemicals (de Serres 1978; Grant 1978; Nilan 1978), this project "Plant Bioassays for the Detection of Chemical Mutagens" was initiated in order to have a different relatively inexpensive mutagen assay system (using higher plants) which would provide a measurement of mutagenic toxicity in assay systems not being carried out by the Ontario Ministry of the Environment. This study involves the use of two higher plants, namely, *Tradescantia* and Barley (*Hordeum vulgare*). Each plant has two different assay systems. The two *Trandescantia* assay systems are: (1) the Stamen Hair Assay for the detection of gene mutations, and (2) the Micronucleus Test for the detection chromosomal aberrations. The two assay systems in barley are: (1) the Root Tip Chromosomal Aberration Assay and (2) the Chlorophyll Mutation Assay. Ethyl methanesulfonate (EMS) is being used as positive control. Tests are being completed on three herbicides, namely, alachlor (Lasso), atrazine, and metolachlor. Preliminary results indicate all three herbicides give a positive response in these plant assays. The herbicide atrazine is strongly mutagenic. The number of mutations from a dose of 50 ppm exceeded the number produced by a 250 ppm dose of EMS used as a positive control. Metolachlor also is mutagenic with the number of mutagenic events from a 240 ppm treatment exceeding the equivalent of 250 ppm EMS. In the stamen hair assay, the mutagenicity of Lasso was not significantly different from the control, however, Lasso caused a high percentage of chromosome aberrations in the micronucleus assay which was double those resulting from a 500 EMS treatment. Lasso also induced fragments in the barley chromosome aberration assay. From the chromosomal data, Lasso is considered to be a strong clastogen. The results to date indicate that higher plant assays are highly suitable for testing for the mutagenicity of environmental chemicals from air, soil and water habitats.

ABSTRACT FORM

Author : D.R. Hart
Address : Beak Consultants Ltd., 6870 Goreway Drive
Mississauga, Ontario Phone (416) 671-2600
Co-Authors : J. Fitchko, M. Brinkman and P.M. McKee

Topic Area : Air ☐, Water ☐, Waste ☐, Analytical ☒

Environmental Economics ☐

Do you prefer presenting: A paper ☒, a poster session ☐

Title: A Biological Indicator System to Identify Genotoxicity of In-Place Pollutants

Abstract:

Morphological abnormalities are often observed in chironomid larvae collected from areas of industrial or agricultural pollution, and have been reported to be more common in these areas than in unpolluted sites. Such observations suggest that chironomid larvae could be useful as indicators of genotoxicity in sediments. However, field studies have not demonstrated correlations between deformity incidence and levels of particular pollutants.

A laboratory study was undertaken to determine whether mouth part abnormalities similar to those observed in the field could be induced by a known genotoxicant, ethyl methane sulfonate (EMS), either in exposed chironomids or in their unexposed offspring.

Abnormal development of the hypostomial plate was induced by chronic embryo-larval treatment with EMS at a nominal exposure level of 240 mg/L, approximately 80% of the chronic LC50 concentration. At this exposure level the deformity incidence (46-50%) was more than doubled relative to controls. Non-significant elevation of deformity incidence was observed at 75 and 100 mg/L, in proportion to the exposure level.

Emergence and reproduction of adults was severely inhibited by EMS embryo-larval exposure levels of 75 and 100 mg/L. At these concentrations few viable adults emerged, and matings between treated males and untreated females produced inviable eggs. Either male infertility or embryonic expression of induced dominant lethal mutations could be responsible.

Emergence and reproduction were apparently normal following embryo-larval exposure to 50 mg/L. However, the incidence of hypostomial deformities in untreated F_1 offspring was increased relative to the exposed parents and relative to concurrent control cultures. This result was based on a single F_1 culture and was not statistically significant.

The incidence of hypostomial deformities in control larvae was variable (5 to 21%) and higher than typically observed in larvae collected from unpolluted field locations. Possible factors contributing to control deformities include physical abrasion of early instar mouthparts, and inbreeding of laboratory cultures. An inbreeding effect was suggested by an increase in control deformity levels over three successive generations.

ABSTRACT FORM

Author : Roger H. Green
Address : Department of Zoology, University of Western Ontario
London, Ontario Phone (519) 661-3127
Co-Authors : Scott G. Hinch and Robert C. Bailey

Topic Area : Air ☐, Water ☐, Waste ☐, Analytical ☒
Environmental Economics ☐

Do you prefer presenting: A paper ☒, a poster session ☐

Title: Freshwater Clams as Monitors of Variation in Environmental Acidity and Trace Metal Levels.

Abstract:

Freshwater clams are commonly used to biologically monitor contaminant levels in aquatic environments. In areas affected by acid rain, trace metal availability to aquatic organisms is enhanced. To help determine the heritability of trace metal uptake rates into clam tissues, we conducted a 3-way reciprocal transplant experiment in south-central Ontario using the unionid clam *Elliptio complanata* and 3 lakes which represent the "degree of acidification" gradient. The effects of transplant source and destination on uptake rates are discussed. Size- and age-specific patterns of trace metal uptake were investigated in these same clams. Irrespective of age, higher levels of Cd and Cu relative to Zn and Mn were found in clams from the more acidic environment. Clam size was generally a good predictor of tissue metal levels suggesting that longterm clam biomonitoring studies should control for size variability.

Although clam tissues are a useful monitor of short-term fluctuations in aquatic contaminant levels, clam shells can be used as indicators of longterm water quality patterns (individual clams can live up to 20 years). Researchers have speculated that small thin shelled clams are characteristic of an environment affected by acidification, since shells are primarily composed of Ca and Ca availability may be low in low alkalinity environments. We examined this theory by sampling *E. complanata* from 4 small lakes of varying alkalinity in south-central Ontario. We determined that most of the differences in shell size and shape were a function of within-lake variation in water turbulence. Therefore the use of shell morphology as a long-term predictor of acidification requires careful consideration of within-lake variability in shell form.

We are using a newly developed image analyser process which is coupled to a micro-computer based digitizer system to investigate patterns of shell erosion which have previously been attributed to increasing acidification. Variability in water turbulence appears to be an equally, if not more, important factor.

ABSTRACT FORM

Author : F.W. Karasek
Address : Dept. of Chemistry, University of Waterloo
Waterloo, Ontario Phone (519) 885-1211, ext. 3423
Co-Authors : T.S. Thompson, D.H. Schellenberg, and K.P. Naikwadi

Topic Area : Air ☐, Water ☐, Waste ☐, Analytical ☒

Environmental Economics ☐

Do you prefer presenting: A paper ☒, a poster session ☐

Title: Analysis of Dioxins and Furans in Fish and Other Biota

Abstract:

The method currently used by the Ontario Ministry of the Environment for the analysis of polychlorinated dibenzo-p-dioxins (PCDD) and dibenzofurans (PCDF) in fish is based on the Dow Chemical cleanup procedure. This method is time consuming and ineffective when high levels of PCB are present. Simultaneous determination of other environmental pollutants such as PCB, PAH, and chlorinated pesticides is not possible because of improper fractionation or poor recoveries. A new procedure has been developed in which the multi-step open column chromatographic cleanup devised by Dow is replaced by a two-step HPLC fractionation.

Fish tissue is digested overnight in concentrated hydrochloric acid and the organic compounds are then extracted with hexane. The organic extract is passed through a sodium sulphate/silica gel column to remove traces of water and lipid material. The resulting extract is then concentrated prior to HPLC fractionation.

Normal phase HPLC using a semi-preparative scale silica column and binary solvent system is used to isolate the PCDD and PCDF from the bulk of the complex organic matrix. Aliphatic hydrocarbons, substituted benzenes, some chlorinated pesticides, three-ring and larger PAH, and polar compounds such as phthalate esters can be fractionated and collected for subsequent analysis. The PCDD and PCDF are eluted along with PCB, chlorinated pesticides, and some substituted naphthalenes. A second step HPLC fractionation is then employed to isolate the PCDD and PCDF from the compounds interfering with their analysis. This separation is carried out using reverse phase HPLC with a C-18 column.

The two-step HPLC fractionation procedure is capable of efficiently removing PCB interferences form PCDD and PCDF even when the levels of the former are greater than 100,000 times that of the latter compounds. In addition, by collecting fractions in both the normal and reverse phase separations it is possible to simultaneously determine a wide range of target compounds from a single fish sample.

ABSTRACT FORM

Author : Cecilia Chan
Address : 5550 McAdam Road, Mississauga, Ontario
L4Z 1P1 Phone (416) 890-2555
Co-Authors : John Martin, Patrick Pond, Gerry Rees and Tony Ho

Topic Area : Air ☐, Water ☐, Waste ☐, Analytical ☒

Environmental Economics ☐

Do you prefer presenting: A paper ☒, a poster session ☐

Title: Development of A Cost-Effective Protocol for Routine Analysis of Trace Organic Contaminants in Municipal WPCP Raw Sewage and Final Effluent.

Abstract:

Further development and improvement of a highly efficient protocol for the detection of trace organics in municipal sewage and final effluent based on the simultaneous in-situ acetylation and extraction is presented. This method provides better sensitivity, allows greater sample throughput and reduces the cost of analysis.

The extraction performance originally based on a target list of chemical parameters chosen to represent various classes of compounds was expanded to include most of the EPA priority pollutants using organic-free water, WPCP raw sewage and final effluent as test substrates. The recovery parameters and their corresponding coefficients of variation prove that the overall protocol is comparable, or in some cases, better than the EPA method 625 for priority pollutant analysis.

Sample analyses were performed on a Hewlett-Packard 5890A Gas Chromatograph coupled with a Mass Selective Detector. Sufficient sample throughput has been achieved through automation of the GC/MSD system and its highly flexible data system. Customized menu-driven software was developed to improve the autosequencing flexibility in sample processing and interpretation, to allow generation of customized reports and implement error checking and quality control routines in the processing.

ABSTRACT FORM

Author : M. Dancziger
Address : 304 Carlingview Drive, Rexdale, Ontario, M9W 5G2
Phone (416) 675-3870
Co-Authors : R. Jackson, L. Danylewych-May and M. Shats

Topic Area : Air ☐, Water ☐, Waste ☐, Analytical ☒

Environmental Economics ☐

Do you prefer presenting: A paper ☒, a poster session ☐

Title: Application of Gas Chromatography with Helium Microwave Plasma Detection to the Rapid Screening of Chemical Wastes

Abstract:

The element specific Helium Microwave Plasma Emission Detector (MED) designed and fabricated by Barringer will be described in this paper. The MED is capable of simultaneously monitoring a pre-selected group of elements such as C, Br, Cl, F, P and S on a low picogram detection level.

The detection system is based on a nine-channel polychromator monitoring the emission from a helium microwave plasma maintained in the Beenakker-type cavity. A gas control unit provided interfacing of the plasma to a Hewlett-Packard 5730 series gas chromatograph. Simultaneous multi-element determination of C, P, Hg, Br, Cl, S and F is achieved with the spectrometer based on a half meter radius concave holographic grating (1180 lines/mm) in a Rowland mounting. The plasma is viewed axially from the open end of the quartz discharge tube. The spectral range from 190 to 800 nm is covered in the first order. Wavelength modulation for background correction is achieved by means of a chopper disc and dual entrance slit. An inert "valveless" GC to cavity interface permits venting of the solvent while passing subsequent GC effluent to the cavity. A gas control unit contains the elements necessary to control the gas flow through the interface (including scavenger gas) as well as electronics to control the transfer line temperature. The interface is capable of supporting both packed column and capillary column chromatography.

Measurements of emission intensity across the diameter of the discharge tube indicated that maximum emission intensity for all elements occurred near the central axis of he tube and this position was independent of plasma power and plasma support gas flow rates. Optimized operating conditions resulted in detection limits of between 1 and 30 pg-sec^{-1} for the elements studied. Attempts to eliminate background levels of nitrogen and oxygen through special gas purification steps and modification to the discharge tube were only partially successful.

The microwave emission plasma detector has successfully demonstrated the capability to be used as a fast screening technique for assessing compounds at trace levels in complex matrices. The intent of this study is to develop a rapid screening technique for target chemical species found in hazardous waste samples without an expensive and time-consuming sample clean-up prior to analysis. Only after this initial screening stage would more costly, high resolution (e.g. GC/MS or GC/ECD) analytical procedures/instrumentation be employed for samples with positive response to target chemical species.

ABSTRACT FORM

Author : G.H. Thomas
Address : Ontario Research Foundation
Mississauga, Ontario Phone (416) 822-4111
Co-Authors : A.J. Horton and K. Matsumura

Topic Area : Air ☐, Water ☐, Waste ☐, Analytical ☒
Environmental Economics ☐

Do you prefer presenting: A paper ☒, a poster session ☐

Title: Development of Methods Suitable for Use in the Ames Salmonella Mutagenicity Assay for the Collection of Organics Present in Groundwater and Landfill Site Matrix Materials.

Abstract:

The objective of the study is to develop methods based on the Ames Salmonella mutagenicity assay to detect potentially harmful contamination of groundwater supplies by genotoxic substances leached from landfill sites. An initial literature review was performed to collect and define existing data available on contaminated groundwater/surface water associated with sanitary landfill and/or hazardous waste disposal operations. From this information a select list of chemicals (including suspected/known mutagens) was compiled which exhibit different functional group features as well as representing a wide range of chemical and physical properties. These chemicals are being used to develop and validate methods for the collection of organic concentrates from both groundwater and site matrix materials in order to provide material suitable for use in the Ames bioassay. The concentration methods are based on accumulator columns (resin adsorption), purging and solvent extraction techniques to determine the range of compounds that can be collected and establish their recovery limits. The organic compounds in the core matrix material (spiked) are being evaluated in terms of their leachability (aqueous, organic and total) compared to the total organic material in the core.

ABSTRACT FORM

Author : E. Lee-Ruff
Address : Dept. of Chemistry, York University, Downsview,
Ontario, M3J 1P3 Phone (416) 736-2100, ext. 3835
Co-Authors : F.J. Ablenas

Topic Area : Air ☐, Water ☐, Waste ☐, Analytical ☒
Environmental Economics ☐

Do you prefer presenting: A paper ☒, a poster session ☐

Title: Synthesis of Oxygen and Sulphur Polynuclear Aromatic Hydrocarbons of Interest in Environmental Pollution

Abstract:

Two novel approaches towards the syntheses of furan and thiophene annelated polynuclear aromatic hydrocarbons (PAHs') have been developed. One of these involve the use of cyclobutanones derived from thienyl ketene additions to olefins or aryl ketene additions to dihydrothiophenes or dihydrofurans. These cyclobutanones are subjected to selective ring opening and cyclization reactions by acid or base to give polycyclic ketones which are modified to the PAHs'. The second approach is the dehydration of thioformidyl aryl methanols under acidic conditions to give terminal PAH thiophenes. Details of both of these approaches will be discussed.

ABSTRACT FORM

Author : Cecilia Chan
Address : 5550 McAdam Road, Mississauga, Ontario
L4Z 1P1 Phone (416) 890-2555
Co-Authors : John Martin, Gerald Ladwig, Gerry Rees and George Crawford

Topic Area : Air ☐, Water ☐, Waste ☐, Analytical ☒

Environmental Economics ☐

Do you prefer presenting: A paper ☒, a poster session ☐

Title: Development of a Robotic Workstation for the Routine Analysis of Organics in Biological Tissues using Acid Digestion and Solvent Extraction Method.

Abstract:

In recent years, laboratory robotic systems have been recognized as a cost-effective means of automating sample processing and reducing human exposure to hazardous chemicals. Automation of sample preparation procedures have also, in general, improved the reliability of the analytical methods and provided higher quality data.

In this work, a Zymate Laboratory Robotic System has been used to develop a workstation for automated processing of fish tissue using an acid digestion and extraction method. Some of the main considerations addressed in this development include the following:

i) Maximization of sample throughput
ii) Comparison of accuracy and precision data using the manual and the automated procedures.
iii) User/operator safety and ease of use.
iv) Flexibility for modification of the developed program along with room for expansion.

In our implementation of the extraction procedures, all sample preparation steps are performed by the robot in modules. Such operations include weighing, dispensing, acid digestion, extraction, centrifugation, dilution, drying, neutralization and calculation.

An IBM compatible personal computer will be interfaced to the robot and its controller for sample input, data, calculation and sample management. Software will be developed to allow the operator greater control of the automated operation, and permit more sophisticated data processing then with only the Zymate Controller. This software will also provide an attractive menu-driven system for sample information, as well as capability for communication with other computers. More in-depth error checking and error recovery routines will also be investigated.

ABSTRACT FORM

Author : K.P. Naikwadi
Address : University of Waterloo, Chemistry Department,
Ontario N2L 3G1 Phone (519) 885-1211 Ext. 3423
Co-Authors : G.M. Charbonneau and F.W. Karasek

Topic Area : Air ☐, Water ☐, Waste ☐, Analytical ☒
Environmental Economics ☐

Do you prefer presenting: A paper ☒, a poster session ☐

Title: Separation and Identification of Organic Compounds in Extracts of Air Particulates by HPLC and GC/MS.

Abstract:

The organic compounds in extracts of air particulate were separated into acidic, basic, and neutral fractions by solvent extraction. The neutral fraction consisted of a large number of aliphatic and aromatic compounds. The identification of aromatic compounds that co-eluted with other compounds was very difficult by gas chromatography alone. Semi-preparative high pressure liquid chromatography (HPLC) was used to separate aliphatic compounds into one fraction and the aromatic compounds in several subsequent fractions. The retention behaviour of aromatic compounds on normal phase columns in HPLC was found to be typical, where capacity factors increased with an increase in the number of rings and was not largely affected by the alkyl substitution or the position of alkyl substitution on a particular aromatic compound. High resolution gas chromatography and mass spectrometry (GC-MS) were used for compound identification. The advantages of acid-base extraction and high pressure liquid chromatography prior to GC-MS analysis are discussed in detail.

ABSTRACT FORM

Author : C.M. Sadowski
Address : York University, 4700 Keele Street, Downsview
Ontario Phone (416) 736-5246
Co-Authors : J. Lai, H. Malle, S.V. Filseth and F.J. Morgan

Topic Area : Air ☐, Water ☐, Waste ☐, Analytical ☒

Environmental Economics ☐

Do you prefer presenting: A paper ☒, a poster session ☐

Title: Quantitative Determination of Selected PAH's by Shpol'skii and Jet-cooled Spectroscopy.

Abstract:

Shpol'skii Spectroscopy has been demonstrated to be a highly selective and sensitive technique in the detection and identification of polynuclear aromatic hydrocarbons (PAH's) in the environment. In this technique a highly dilute solution of the sample in a solvent, such as n-octane, is added to a cell and cooled to a temperature of about 12K. The frozen matrix is illuminated with a laser and the resulting fluorescence is observed with a photomultiplier-monochromator combination. Two types of spectra are obtainable - a fluorescence spectrum in which the sample is illuminated at a fixed laser frequency whilst the fluorescence is scanned with a monochromator, and an excitation spectrum in which the fluorescence is observed in a fixed wavelength interval whilst the excitation frequency provided by a turntable laser is scanned. This technique can be easily adapted to quantitative analysis, because the peak heights of the quasi-lines generated by the Shpol'skii spectroscopic technique are proportional to the concentration of a given PAH provided that the signal does not saturate the photomultiplier and the laser intensity is not so high as to cause significant depletions of the ground state population. An additional requirement is that the concentrations used be low enough to minimize solute-solute interactions. Once a suitable quasi-line is selected, it is possible to obtain a calibration curve relating to the peak height normalised by the laser energy to the concentration of the PAH in a prepared solution in n-octane. In this paper results will be presented of the quantitative determination of benzo(a)pyrene in a number of environmental samples.

A complementary technique is that of Jet-cooled Spectroscopy. Here the sample is heated in an oven to generate a usable vapour pressure of the PAH. This vapour is subsequently mixed with helium or argon and the mixture is expanded into a chamber maintained at a low pressure by fast pumping. The gaseous mixture enters this chamber in the form of a free or over-expanded jet that is cooled by the strong adiabatic expansion to cryogenci temperatures. For example, 50 or so nozzle diameters downstream of the nozzle a rotational temperature of approximately 5-7K is obtained. At such low temperatures only the lowest rotational levels of the lowest vibronic state are significantly populated, and the absorption spectrum is thereby greatly simplified. Excitation spectra obtained by this technique resemble those obtained by Shpol'skii spectroscopy, but are shifted relative to the other in wavelength. This shift arises form the fat that in a matrix there are strong interactions between the PAH and the solvent molecules, whereas in a molecular jet beam the PAH molecules are virtually isolated. The proportionality between peak height and beam density under the same restrictions as discussed above permits the quantitative determination of PAH's. In this paper Jet-cooled spectra of selected PAH's will be presented as well as a progress report on the quantification of the beam technique.

ABSTRACT FORM

Author : Victor A. Snieckus
Address : Chemistry, University of Waterloo, Waterloo,
Ontario, N2L 3G1 Phone (519) 888-4007
Co-Authors :

Topic Area : Air | |, Water | |, Waste | |, Analytical |x|

Environmental Economics | |

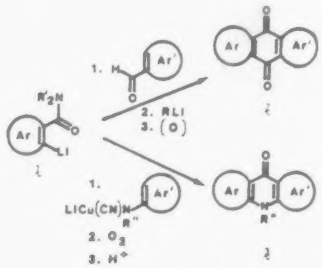
Do you prefer presenting: A paper |x|, a poster session | |

Title: New Synthetic Methodology for the Expedient Provision of Isomerically Pure PAH Analytical Standards.

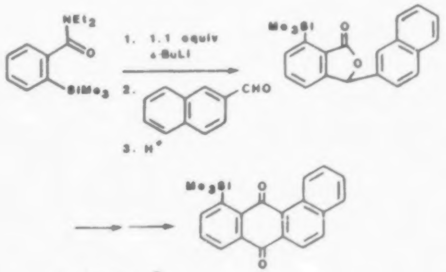
Abstract:

Recent work in our laboratories has been focused on the application of the directed ortho metalation reaction **Scheme** 1) for the synthesis of a variety of PAHs and aza-PAHs of environmental interest. The increasing need for rapid and efficient access to diverse PAHs for analytical standards and for carcinogenesis research provides the impetus for the continuation of our efforts in this area. Extension of the aromatic directed metalation strategy to the synthesis of previously inaccessible halo- and methyl-PAHs by using silicon protection tactics will be described.

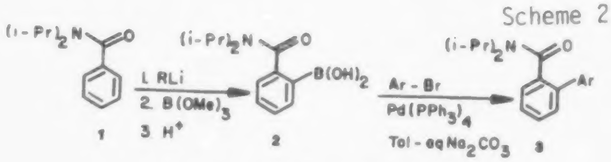
Accumulating evidence that the highly mutagenic nitro-PAHs are widely distributed in the environment has stimulated the application of methods discovered recently in our laboratories towards their synthesis. New syntheses of silylated PAHs (**Scheme** 2) and nitro-biphenyls (**Scheme** 3) will be presented and the evaluation of these compounds as precursors to nitro-PAHs will be reported.



Scheme 1



Scheme 2



Scheme 3

SESSION E

ENVIRONMENTAL ECONOMICS

ABSTRACT FORM

Author : Clifford Russell
Address : Vanderbilt University, Nashville, Tenn., USA
Phone (615) 322-8505
Co-Authors :

Topic Area : Air ☐, Water ☐, Waste ☐, Analytical ☐
Environmental Economics ☒

Do you prefer presenting: A paper ☒, a poster session ☐

Title: "The Environment of Economics - Past, Present and Future Roles of Economics in Environmental Management."

Abstract:

It is doubtful that there exists an area of public policy in which a clearer case can be made for the necessity of interdisciplinary approaches to problem analysis and policy design than the area of environmental quality management. Yet this case is regularly ignored on both sides of the line dividing economics from other relevant disciplines, including the life, chemical, and physical sciences, other social sciences, and certain of the humanities. There is fault enough on both sides of this situation. But the purpose of this paper is not to apportion blame; rather it is to catalog the contributions that economics, in cooperation with other disciplines, can make to environmental policy.

Those contributions may be subsumed within four broad areas:

- critically examining often conflicting claims about the need for any government policy (or conversely, about the desirability of "deregulation")
- predicting the effects, especially the indirect effects, of particular policy suggestions
- estimating the costs and benefits associated with particular policies -- either before or after implementation -- as an input to the decision process
- analyzing implementation problems, and designing positive and negative incentive systems, and accompanying monitoring and enforcement activities.

In the process of expanding on this catalog, the paper will comment on the actual and potential interaction among the disciplines.

ABSTRACT FORM

Author : J.A. Donnan
Address : Ontario Ministry of Environment, 135 St. Clair Avenue W.
Toronto, Ontario Phone (416) 965-0641
Co-Authors : C. Griffith, S. Glover, M. Dandele

Topic Area : Air ☐, Water ☐, Waste ☐, Analytical ☐
Environmental Economics ☒

Do you prefer presenting: A paper ☒, a poster session ☐

Title: "Abatement Cost Functions - The Workhorse of Environmental Management"

Abstract:

Abatement cost functions are tables or algebraic statements which relate varying levels of pollutant treatment or reduction to the costs (in monetary terms) of achieving them. Abatement cost functions may be developed for a wide variety of control technologies, production processes, industrial establishments or for specific pollutants or contaminants. Abatement cost functions have been extremely useful tools for:

1. assessing the costs and financial impacts of achieving specific emission objectives,
2. determining the implications of different enforcement policies,
3. predicting a firm's reaction to particular environmental objectives,
4. developing cost-effective abatement programs,
5. conducting benefit-cost analyses,
6. evaluating abatement programs after they have been implemented.

Methods for developing abatement cost functions will be critically reviewed. A computer program called the Waste Treatment Analysis Program (WATAP), developed by the Ministry to generate abatement cost estimates, will be highlighted.

Examples of how abatement cost functions have been derived and applied in specific cases will then be presented. These case studies include nickel smelters, lime plants, and electric power plants in Ontario.

ABSTRACT FORM

Author : Paul M. Wiancko
Address : Ontario Hydro, Toronto, Ontario
Phone (416) 592-4599
Co-Authors : Barry A. Green

Topic Area : Air ☐, Water ☐, Waste ☐, Analytical ☐
Environmental Economics ☒

Do you prefer presenting: A paper ☒, a poster session ☐

Title: "Measuring the Social Costs of Electrical Exports and Cost Recovery Opportunities of Environmental Protection at Ontario Hydro."

Abstract:

In its efforts to compensate for environmental impacts, Ontario Hydro recovers social costs from electrical export sales as well as private costs from the sale of by-products from its operations.

The National Energy Board (NEB) of Canada requires evidence in applications for electrical export licenses that the price charged would recover an appropriate share of the total cost incurred in Canada. Social costs that result from emissions from fossil fuel plants that can be attributed to exports are a component of the cost to Canada of electrical exports.

It is a policy of Ontario Hydro to add a social cost surcharge to the price of electrical exports to the United States.

Environmental effects on sensitive receptors in Canada (and estimates of their monetary value) that result from fossil fired air emissions were originally produced in 1974 and updated in 1980-81. For both these studies, consultants reviewed the literature on the effects of SO_2 and particulate emissions on human health, building materials, textile products, water quality, vegetation, animals, and property values. Based on the 1980-81 report updates, the social cost "adder" or surcharge was estimated to be $0.40/megawatt hour.

Ontario Hydro has a commitment to the NEB to continuously review the social cost studies and periodically revise the social cost "adder". The literature was again reviewed in 1984. This latest review updated the potential impacts on human health, aquatic and terrestrial ecosystems, structural materials, and property values. The estimated value of the social cost was similar to the 1980-81 values and suggests a value in the range of 0-$0.50/megawatt hour.

The results of this recent literature review, the methodology for calculating social costs and the estimates of the values for the various sensitive receptors will be presented.

In addition, Ontario Hydro recovers environmental protection costs by selling by-products such as fly ash, timber, isotopes and waste oils.

ABSTRACT FORM

Author : Claude Sauvé, Ministry of the Environment
Address : 2360 Chemin Ste-Foy
Sainte-Foy, Quebec Phone (418) 643-1852
Co-Authors :

Topic Area : Air ☐, Water ☐, Waste ☐, Analytical ☐

Environmental Economics ☒

Do you prefer presenting: A paper ☒, a poster session ☐

Title: "Quebec's Experience with the Economic Evaluation of Environmental Regulations - What Lessons have been Learned?"

Abstract:

The Government of Quebec introduced, in 1981, the requirement to evaluate the economic implications of new regulations of all kinds that may have an effect on industry. This requirement applies in particular to legislation of a social character and especially regulations having an impact on the environment.

The implementation of this requirement continues to pose problems regarding methodology, organization, and at times, even problems of a purely technical nature. For example, these evaluations have, in many cases, strengthened the decision-making process.

What has been the effect of economic evaluations in the development of regulations, their adoption and their environmental effectiveness? In what manner have these evaluations facilitated Government decision making in the area of environmental protection? What role should these evaluations have in the context of the present economic climate?

ABSTRACT FORM

Author : Claude Sauvé, Ministère de l'Environnement
Address : 2360 Chemin Ste-Foy
Sainte-Foy, Québec Phone (418) 643-1852
Co-Authors :

Topic Area : Air ☐, Water ☐, Waste ☐, Analytical ☐
Environmental Economics ☒

Do you prefer presenting: A paper ☒, a poster session ☐

Title: "L'expérience du Québec en matière d'évaluation économique des réglementations environnementales: Quelle leçon peut-on en tirer?

Abstract:

A l'instar d'autres entités gouvernementales, le gouvernement du Québec a introduit, en 1981, l'obligation d'évaluer les implications économiques des nouvelles réglementations qui ont des impacts sur les entreprises. Cette obligation a particulièrement touché les legislations à caractère social et notamment les réglementations de nature environnementale.

La réalisation de ces évaluations a posé et continue de poser des problèmes méthodologiques, organisationnels et souvent purement techniques. Par ailleurs, ces évaluations ont dans plusieurs cas alimenté le processus décisionnel.

Quelle a été la portée réelle de ces évaluations sur la formulation des règlements, leur adoption et leur efficacité environnementale? Dans quelle mesure ces évaluations ont-elles fourni un meilleur éclairage à la prise de décision gouvernementale en matière d'environnement? Quel rôle devraient jouer ces évaluations dans le présent contexte économique?

ABSTRACT FORM

Author : A.G. Mills
Address : 3M Canada Inc. P.O. Box 5757, London, Ontario
N6A 4S7 Phone (519) 452-6203
Co-Authors :

Topic Area : Air | |, Water | |, Waste | |, Analytical | |

Environmental Economics |x|

Do you prefer presenting: A paper |x|, a poster session | |

Title: 3M's Pollution Prevention Pays Program

Abstract:

This paper describes a program devised by the 3M Company to reduce or eliminate pollution in its operations and at the same time, improve the environment, conserve resources, improve technologies and reduce costs.

It illustrates how corporate policy has helped shape the program and in addition, provides examples of how pollution elimination has been achieved through product reformulation, process modification, equipment redesign and productive use of waste materials.

Finally, it describes the importance of 'communication' for maintaining a high profile for the program and as the essential ingredient for its success.

A summary of 'results' is also provided.

ABSTRACT FORM

Author : Ronnie Levin
Address : U.S. Environmental Protection Agency, 402 Main Street S.W.
Washington, D.C. 20460 Phone (202) 382-2784
Co-Authors :

Topic Area : Air ☐, Water ☐, Waste ☐, Analytical ☐
Environmental Economics ☒

Do you prefer presenting: A paper ☒, a poster session ☐

Title: "The Benefits of Reducing Lead in U.S. Drinking Water"

Abstract:

The U.S. EPA has proposed to reduce the maximum contamination level (MCL) for lead in drinking water by 60%, from 50 ug/l to 20 ug/l. To support this proposed rule, the Agency has undertaken a major study to determine (a) the current public exposure to lead in U.S. drinking water, (b) the adverse health effects associated with these levels, (c) the potential reductions in these adverse effects from this proposed rule, (d) other benefits associated with reducing lead in drinking water, and (e) the monetary value of these benefits. Data on the costs are available.

Lead occurs in drinking water primarily as a corrosion by-product. Its main sources are the materials of the distribution and residential plumbing systems. While the presence of lead pipes is relatively restricted geographically, the use of lead solder is ubiquitous. The combination of copper pipes with lead solder found in most residences can result in high lead levels which exceed the current MCL, even with the use of fairly non-corrosive waters. Newly installed solder is extremely soluble, and new housing is at particular risk of high lead levels. We used a variety of public and private sources of data on the parameters of U.S. drinking water, combined with projections of residential construction, to determine the current public exposure to lead in public water supplies.

Lead has long been known to cause a wide range of pathologic and physiological effects, ranging from subtle biochemical changes to severe retardation and even death, at very high levels. From among lead's many adverse health effects in children, we calculated the potential benefits of reducing the medical treatment costs to lower the body lead burden for children with elevated lead levels and developed two alternative methods for valuing cognitive damage resulting from lead exposure. In addition, we calculated the reduction in the number of children at risk from several other health effects as a result of this proposed rule, but without ascribing any monetary value to those benefits.

Several recent articles have shown a continuous relationship between blood lead and blood pressure levels. To calculate the benefits of reduced lead exposure, we used logistic regression equations to predict how the proposed rule would affect blood pressure levels, and from that, estimated expected reductions in the numbers of hypertensives, heart attacks, strokes, and deaths. We used published materials on the medical cost of these events to monetize the benefits. We also discuss but ascribe no monetary value to some of lead's reproductive effects.

Because lead is present in drinking water primarily as a corrosion by-product, corrosion control treatment is the preferred treatment for reducing it. The resultant reduction in corrosion damage will produce substantial materials benefits.

The annual net value of the benefits of reducing lead in U.S. drinking waters is estimated to be about $800 million, for sample year 1988.

ABSTRACT FORM

Author : J.M. Callaway
Address : P.O. Box 999, Richland, WA, 99352
Phone (509) 376-4741
Co-Authors : R.F. Darwin

Topic Area : Air ☐, Water ☐, Waste ☐, Analytical ☐

Environmental Economics ☒

Do you prefer presenting: A paper ☒, a poster session ☐

Title: Economic Effects of Reduced Forest Growth on the United States' Forest Economy and on Canadian-U.S. Lumber Trade

Abstract:

Several recent studies have reported both localized and region-wide decreases in the radial growth rates of several commercially important forest species in the eastern half of the United States. These observed reductions in tree growth rates may be related to increases in acid deposition and other man-made air pollutants over the last three decades. In the first part of this study, we review the evidence regarding these reductions in forest growth and, using economic theory, show how these physical changes can impact the production and purchasing decisions of buyers and sellers in timber and primary wood product markets. We then show how standard willingness-to-pay principles can be used to place monetary values on the physical damages caused by air pollution, due to these changes in the behaviour of economic agents in affected markets. In the second part of the study, we describe how this information about changes in tree growth can be used in conjunction with existing inventory projection and timber market models to simulate the potential economic effects of acid deposition/air pollution in the United States. Two sets of simulations are conducted. The first set assumes that air pollutants generated in the United States do not damage Canadian forests. The second set of simulations attempt to take into account the potential effects of reduced growth in Canadian forests due to air pollutants generated in the United States. These damages are simulated by increasing Canadian stumpage fees in the Canadian lumber supply functions contained in the timber market model used in the analysis. The final part of the study presents the results of the simulations, quantifying the potential economic effects of acid deposition in the United States and, to a limited extent, Canada. Specific attention is focused on the effects of different assumptions regarding the magnitude and geographic distribution of reduced tree growth on timber inventories, stumpage prices and harvest levels, lumber and plywood production and prices in the United States, and on Canadian lumber exports to the U.S. Estimates of the effects of reduced tree growth on the welfare of timber owners and the buyers and sellers of lumber and plywood in the United States are presented, along with information about changes in the welfare of lumber producers in Canada. These results suggest that if increases in Canadian stumpage fees (as a government response to transboundry pollution damage) are not too great, Canadian lumber producers and exporters may actually earn higher profits because of increased lumber demand from the United States. Finally, the study comments on the significance of these impacts vis-a-vis proposed emission reduction measures in the United States and suggests future directions for research.

ABSTRACT FORM

Author : R. Andrew Muller
Address : Department of Economics, McMaster University
Hamilton, Ontario Phone (416) 525-9140 Ext. 3831
Co-Authors :

Topic Area : Air ☐, Water ☒, Waste ☐, Analytical ☐

Environmental Economics ☒

Do you prefer presenting: A paper ☒, a poster session ☐

Title: "Some Economics of the Grand Canal"

Abstract:

This paper uses a cost-benefit framework to organize a discussion of the economics of the Grand Canal project. This scheme calls for the conversion of all or part of James Bay into a freshwater lake which would accumulate run-off from northern rivers in Ontario and Quebec. The water would be pumped south to the Great Lakes for consumption, export and stabilization of lake levels.

The estimated costs and benefits are very crude. Nevertheless, the exercise has been useful in judging the feasibility of the project and in identifying issues of critical importance. On the basis of available information, the Grand Canal scheme seems to be quite unviable. Estimated net benefits are a small fraction of estimated costs, even before quantification of social and environmental costs and the opportunity cost of the water itself. To reverse this assessment would require clear identification of a large potential market for exported water and a well specified engineering plan to deliver the water at costs below those now contemplated.

The cost-benefit framework proves useful in organizing our discussion and in emphasizing the importance of realistic estimates of potential markets. The techniques developed by cost-benefit analysts help to avoid the misuse of economic impact assessment and to avoiding excessive emphasis on the employment creation aspect of the scheme.